THE EQUILIBRIUM BETWEEN MOLTEN IRON AND FeO-MnO-SiO_2 SLAGS

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by

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INTRODUCTION.

INTRODUCTION.

The manufacture of steel from pig iron and scrap is an oxidation process in which impurities such as phosphorus, carbon and silicon are oxidised and taken into the slag. During this process the molten metal dissolves oxygen to an extent which depends on the composition and temperature of the metal and slag. Normally the amount of oxygen dissolved in the steel at the end of refining is in excess of that desired and before the metal is teemed this excess must be removed. The amount of deoxidation necessary depends on the quality of steel and on the type of ingot which is to be produced. Thus rimming steels are not as fully deoxidised as killed steels.

There are three different methods of deoxidation, namely, diffusion deoxidation, carbon deoxidation and precipitation deoxidation. Diffusion deoxidation which is practiced in electric steelmaking involves covering the molten metal with a slag containing only a very small amount of ferrous oxide. This slag being out of equilibrium with the molten metal will remove ferrous oxide from the metal till equilibrium is attained. In deoxidation by carbon the deoxidation product is carbon monoxide which can be relatively easily removed from the metal. Precipitation deoxidation is the most widely practiced method and is used almost exclusively in the open hearth and converter steelmaking processes. In this method, elements having greater affinities for oxygen than iron are added to the steel. In addition to removing oxygen from the steel these elements must give products of reaction which can rapidly separate from the molten metal. The requirements of a good deoxidiser are:-

(a) Higher affinity for oxygen than iron

(b) Rapid solution in liquid iron.

(c) High rate of reaction with oxygen dissolved in iron.

(d) Rapid rise of the products of reaction.

The most commonly used elements are manganese, silicon and aluminium and these satisfy the first three requirements.

The rate of rise of the deoxidation products in liquid steel increases as the size of the product increases and also the nearer the shape approaches to a sphere. If the deoxidation product is a liquid it can increase its size by coalescing with other particles and will also tend to be spherical, whereas if the product is solid, it is unable to coalesce with other particles and is usually irregular in shape. Thus wherever possible deoxidisers should be chosen which give liquid deoxidation products. The latter are more likely to result from the use of alloys than single elements.

The study of the oxygen content of iron in equilibrium with liquid oxides which may be produced during deoxidation is thus very important from the point of view of understanding and improving deoxidation practice. Thermal equilibrium diagrams indicate slag compositions which will be liquid at steelmaking temperatures, and by performing slag/metal melts with these slags the relation between the metal composition and the deoxidation product can be determined. In this work a study has been made of deoxidation using manganese and silicon. The approach has been to determine the equilibrium between molten iron and iron manganese silicates. Deoxidation using manganese and silicon is one of the most

widely practised methods in steelmaking. Before deoxidation can be completely understood and placed on firm scientific bases many investigations of this type will be necessary. Calculations can then be made to find the best deoxidation alloy to use for any particular purpose and the amount necessary to achieve any given degree of deoxidation.

DISCUSSION OF PREVIOUS WORK.

II. DISCUSSION OF PREVIOUS WORK.

1. Oxygen Solubility in Liquid Iron.

The phase diagram of the iron-oxygen system(1) is shown in Fig.1. This shows an immiscibility gap in which the two phases are liquid iron containing dissolved oxygen and a liquid oxide phase. The latter has a variable composition but is always slightly richer in oxygen than would be represented by the formula FeO. Richardson(2) has given it the formula $Fe_{0.95}O$ and its free energy of formation as

$$0{\cdot}95Fe_{(L)} + \tfrac{1}{2}O_2 = Fe_{0.95}O_{(L)} \quad \Delta G^\circ = -59{,}050 + 12{,}85T.$$

In discussions on steelmaking reactions the phase is normally referred to as ferrous oxide and will be treated as such in this discussion. The boundary BC gives the composition of the metal phase in equilibrium with the liquid oxide phase. It also marks the limit of solubility of oxygen in liquid iron, as once this oxygen content is reached at any given temperature a liquid oxide phase appears.

Many determinations of this limiting solubility of oxygen in iron have been made. In all these investigations impurities have been present in the oxide phase because of the inherent experimental difficulty of obtaining a container which will not be attacked by molten iron or by the oxide phase.

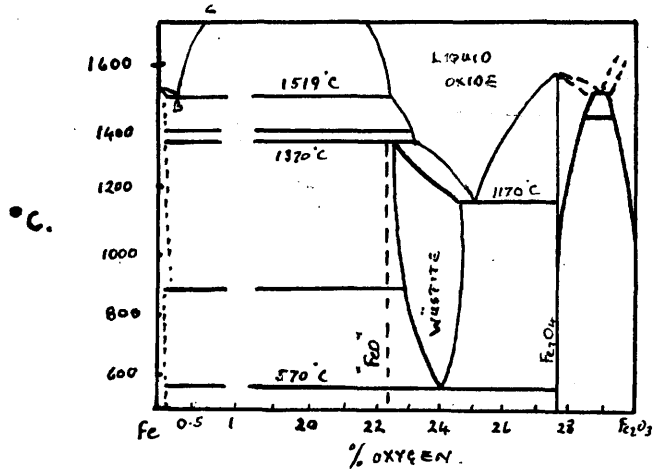


FIG 1a IRON-OXYGEN SYSTEM (WHITE[1])

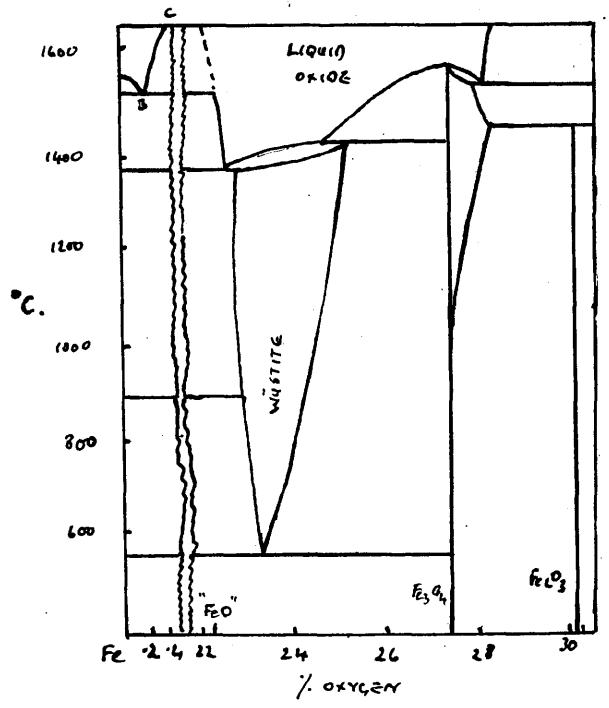


FIG 1b IRON-OXYGEN SYSTEM (DARKEN AND GURRY[1])

Le Chatelier(3) reported a solubility of oxygen in iron as 0·244% at 1600°C. Austin(4) using magnesia crucibles found the solubility to be 0·288% but did not state a temperature. Tritton and Hanson(5) found the solubility to be 0·21% at the melting point of iron.

Herty and Gaines(6) made the first study of the effect of temperature on the solubility of oxygen in iron and gave the solubility as

$$[O]_{Fe_{(max)}} = 0{\cdot}1475\ 10^{-2} T°C - 2{\cdot}038$$

which gave a solubility of 0·25% at 1550°C.

Körber and Oelsen(7) measured the oxygen content of iron melts made under FeO-MnO-MgO slags. They found that the oxygen content of these melts was directly proportional to the ferrous oxide content of the slags and by extrapolating to 100% ferrous oxide found the solubility of oxygen in iron at different temperatures. They found this solubility to be

$$[O]_{Fe_{(max)}} = 0{\cdot}131\ 10^{-2}\ t°C - 1{\cdot}77$$

giving a solubility of 0·26% oxygen at 1550°C. This figure was in agreement with that of Herty and Gaines.

Chipman and Samarin(8) by studying the equilibrium between molten iron and a hydrogen-water vapour gas mixture found that the concentration of oxygen in liquid iron was proportional to the ratio $\frac{p_{H_2O}}{p_{H_2}}$ and hence to the partial pressure of oxygen. Thus a solution of oxygen in iron obeys Henry's Law up to saturation and its activity is directly proportional to its concentration.

Dastur and Chipman(9) using a more refined experimental technique than Chipman and Samarin have measured the standard free energy charge for a solution of oxygen in iron.

$$\tfrac{1}{2}O_2 = [O]_{1\%\text{ activity in liquid iron}}$$

$$\Delta G^\circ = -27{,}930 - 0{\cdot}57T \text{ cal.}$$

An investigation of the solubility of oxygen in iron has been made by Chipman and Fetters(10) using magnesia crucibles and heating in a high frequency induction furnace. The slags consisted mainly of ferrous oxide with small amounts of magnesia and calcium oxide picked up from the crucible. They found a much lower solubility than that obtained by Körber and Oelsen(7) and Herty and Gaines(6), reporting it as

$$\log \%\text{ oxygen} = \frac{-4860}{T} + 1{\cdot}935$$

giving a solubility of 0·19% at 1550°C.

This solubility was found to be independent of the nature of the furnace atmosphere and of the purity of the ferrous oxide slag when its total FeO content was above 90%. Chipman and Fetters also found that ferric oxide was not completely reduced to ferrous oxide by molten iron but that the ratio of $\frac{Fe_2O_3}{FeO}$ in their slags at the melting point of iron was 0·072. This was slightly higher than the ratio 0·055 reported by Darken(11) for ferrous oxide slags melted in iron crucibles. The presence of magnesia in the slags possibly increased the ferric oxide content by stabilising ferrites.

Sloman(12) found the solubility of oxygen in iron at its melting point to be 0·15% which agreed with the value of Chipman and Fetters and disagreed with that of Körber and Oelsen and Herty and Gaines.

Chipman and Taylor(13) using a rotating crucible furnace with magnesite crucibles checked the data of Chipman and Fetters(10). They found the solubility of oxygen in iron to be

$$\log \% \text{ oxygen} = \frac{-6320}{T} + 2{\cdot}734$$

giving a solubility of 0·19% at 1550°C. This work gave results of the same order as those of Chipman and Fetters, only differing at higher temperatures as indicated in Fig.2.

Fischer and vom Ende(14), who also used a high frequency furnace with magnesite crucibles, redetermined the solubility of oxygen in iron and reported a value of the same order as Chipman and Fetters and Chipman and Taylor; their results are shown in Fig.2.

The most probable cause of the discrepancies between the values obtained by Körber and Oelsen(7) and Herty and Gaines(6) on the one hand and Chipman and his co-workers(10,13), and Fischer and vom Ende(14), on the other, is the different methods used for temperature measurement as Chipman and his co-workers(10,13) have shown that the effect of differing atmospheres and sampling techniques cannot be the cause. Körber and Oelsen and Herty and Gaines used optical pyrometers for temperature measurements whereas Taylor and Chipman, and Chipman and Fetters used immersion thermocouples. Optical pyrometers would be inaccurate due to the absence of black body conditions and the volatilisation of ferrous and manganous oxides. Although Körber and Oelsen used emission coefficients to adjust their temperature readings it would appear that their temperature measurements were still too low, and that this led to higher values of oxygen solubility.

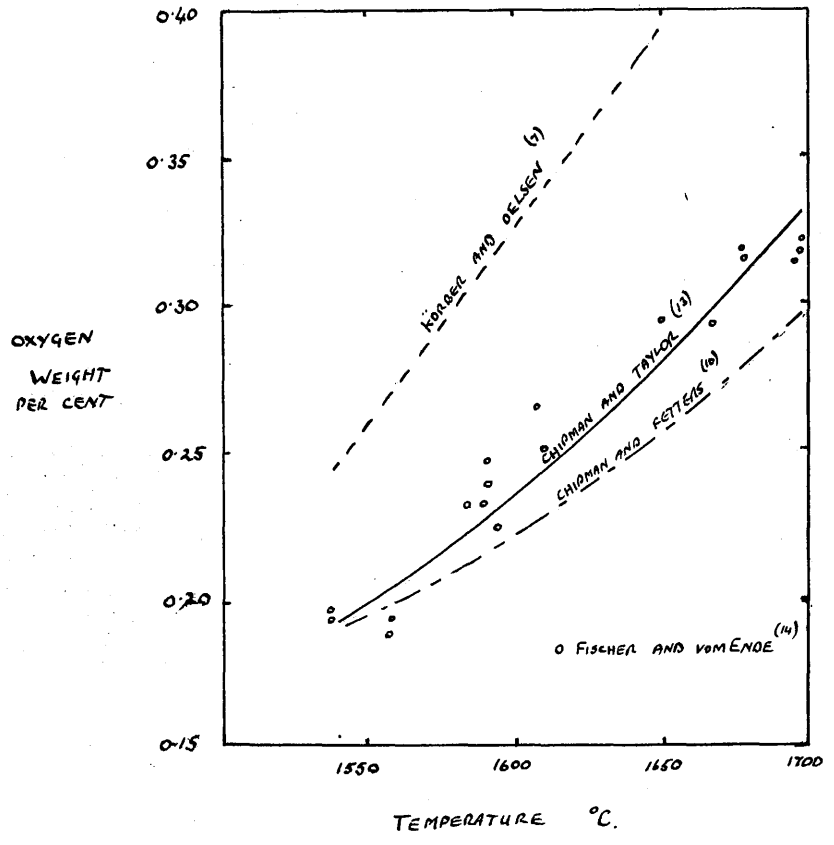


FIG. 2 EFFECT OF TEMPERATURE ON SOLUBILITY OF OXYGEN IN LIQUID IRON.

2. Manganese and Oxygen equilibrium in liquid iron.

The stable oxide of manganese in contact with liquid iron is manganeous oxide (MnO). The free energy of formation of manganous oxide(15) is

$$Mn_{(L)} + \tfrac{1}{2}O_2 = MnO_{(S)} \quad \Delta G = -95{,}400 + 19{\cdot}62T \text{ cal.}$$

Ferrous oxide and manganous oxide are completely miscible in the liquid state but evidence on the solid structure of the mixed oxide is still conflicting. Hay, Howat and White(16) and Benedicks and Löfquist(17) have published diagrams showing a two phase region in the solid state while Andrew, Maddocks and Howat(18) and Herty and Daniloff(19) have indicated that ferrous oxide and manganous oxide are completely miscible in the solid state. Jay and Andrews(20), Pettersson(21) carried out an X-ray study of the solid state and found only one phase present throughout the system. Carter, Murad and Hay(22) have provisionally accepted the evidence of complete solubility in their discussion of the FeO-MnO-SiO_2 system. Sloman and Evans(23) and Whiteley(24) by examining FeO-MnO inclusions from steel find no evidence of immiscibility in the inclusions. The weight of evidence is in favour of complete miscibility in both the liquid and solid state but as yet no reliable diagram showing the liquidus and solidus has been published. The appearance of a two phase region in the work of Hay, Howat and White may have been due to the formation of ferrites in the slags. Darken and Gurry(25) have shown in experiments on the Mn-Fe-O system that MnO has almost as great an influence as CaO in stabilising Fe_2O_3.

When manganese is introduced into liquid iron containing oxygen, the equilibrium is

$$(FeO) + [Mn] = (MnO) + Fe \qquad K = \frac{(a_{MnO})}{(a_{FeO})\,[a_{Mn}]}$$

The activity of iron is taken as unity in the concentrations occurring in steelmaking. When weight percentages are substituted for activities the constant has been designated

$$K'_{Mn} = \frac{(\%MnO)}{(\%FeO)\,[\%Mn]}$$

As MnO and FeO are similar and are assumed to be completely miscible in both the liquid and solid states, their activities can be replaced by concentrations and because of their similarity in molecular weight, by weight concentrations. This gives

$$100\,K'_{Mn} = K$$

and the equilibrium constant K'_{Mn} can be taken as the true equilibrium constant K_{Mn} for the manganese reaction if the slag consists almost entirely of ferrous and manganous oxides.

A value for this equilibrium constant can be calculated from fundamental thermodynamic data.

$$Mn_{(l)} + \tfrac{1}{2}O_2 \rightleftharpoons MnO_{(s)} \qquad \Delta G = -95{,}400 + 19{\cdot}62T \text{ cal.} \qquad (15)$$

$$Fe_{(l)} + \tfrac{1}{2}O_2 \rightleftharpoons FeO_{(l)} \qquad \Delta G = -56{,}830 + 11{\cdot}94T \text{ cal.} \qquad (15)$$

$$MnO_{(s)} \rightleftharpoons MnO_{(l)} \qquad \Delta G = +10{,}700 - 5{\cdot}2T \text{ cal.} \qquad (15)$$

Assuming that a solution of manganese in iron behaves ideally then

$$Mn_{(l)} \rightleftharpoons [Mn]_{1\%\text{ soln. in Fe.}} \qquad \Delta G = RT \ln 0{\cdot}01$$

$$= -9{\cdot}15T \text{ cal.}$$

Hence

$$[Mn]_{1\%} + FeO(\ell) = MnO(\ell) + Fe(\ell) \quad \Delta G = -27,870 + 11{\cdot}63T \text{ cal.}$$

$$\ln K = \frac{-\Delta G}{RT} = \frac{27,870 - 11{\cdot}63T}{4{\cdot}575T}$$

$$\log K_{Mn} = \frac{6080}{T} - 2{\cdot}54$$

at 1550°C $K_{Mn} = 6{\cdot}1$

The accuracy of this calculated constant depends on the accuracy of the thermodynamic data and the errors in these are large enough to have a considerable effect on this constant. Gero, Winkler and Chipman(26) carried out a similar calculation based on slightly different data and calculated a constant of

$$\log K_{Mn} = \frac{6440}{T} - 2{\cdot}82$$

at 1550°C $K_{Mn} = 5{\cdot}1$

which is considerably lower than the value calculated above.

Several investigations of the manganese equilibrium have been made. Krings and Schackmann(27) carried out melts in small alumina and magnesia crucibles, their slags thus containing either magnesia or alumina as impurities. The results from melts made in magnesia or alumina showed no significant differences. They reported a value for K_{Mn} of $3{\cdot}1 \pm 0{\cdot}2$ at 1550/1560°C. Körber and Oelsen(7) used a small high frequency furnace with magnesia crucibles, measuring the temperature with an optical pyrometer. Quench samples were obtained by dipping a spoon into the slag and metal. The results were summed up in the equation

$$\log K_{Mn} = \frac{6234}{T} - 1{\cdot}0263$$

which correspond to a K_{Mn} of 2·5 at 1550°C.

Gero, Winkler and Chipman(26) have re-examined the manganese equilibrium using data from melts made by Winkler and Chipman(28). These melts were made in a large magnesia crucible the metal being heated by induction and the slag by an electric arc held above the melt. The slags consisted of ferrous and manganous oxides with magnesia, silica and calcium oxide as impurities. From this data Gero, Winkler and Chipman calculated two values of K_{Mn}, one using the total ferrous oxide content of the slag (ΣFeO) and the other only the actual FeO content as determined by analysis, and designated $K^{\pm}_{Mn}$. The values obtained were

$$\log K_{Mn} = \frac{6440}{T} - 2{\cdot}95$$

$$\log K^{\pm}_{Mn} = \frac{6760}{T} - 2{\cdot}98 \qquad (7)$$

These values of K_{Mn} differed considerably from those of Körber and Oelsen and are compared with those of other workers in Table I.

Table I. Values of K_{Mn} at 1550°C.

Ref.	Körber and Oelsen(7)	Krings and Schackmann(27)	Gero Winkler and Chipman(26)	
			K_{Mn}	$K^{\pm}_{Mn}$
K_{Mn}	2·4	3·1	3·8	5·2

The low value found by Körber and Oelsen is probably due to the use of optical pyrometers.

The oxygen data of Winkler and Chipman and Körber and Oelsen showed that ferrous oxide behaved ideally in an FeO-MnO-MgO slag, as the ratio $\frac{[\%O]}{(FeO)}$ was independent of the slag composition and depended only on temperature.

Hilty and Crafts (29) attempted to check the equilibrium constant K_{Mn} using a furnace with a rotating crucible, and found that an FeO-MnO slag would not remain in the rotating metal cup, but crept up the sides of the crucible on rotation. They were only able to report their results as a relation between the oxygen and manganese contents of the liquid iron. This data agreed with those of Winkler and Chipman but not with those of Körber and Oelsen. The three sets of results are compared in Fig.3.

Sloman and Evans(23) studied the deoxidation of iron by manganese at the melting point of iron, by adding a known amount of iron oxide followed by a weighed amount of manganese to liquid iron held in an alumina crucible in an argon atmosphere. The melt was analysed for manganese and oxygen and the inclusions separated by the alcoholic iodide method for X-ray analysis. This investigation did not lend itself to the determination of K_{Mn} in liquid iron but for comparative purposes Sloman and Evans assumed equilibrium to be attained at the melting point of iron (1527°C). Their results agreed fairly well with the theoretically determined equilibrium between iron and solid FeO-MnO slags as calculated by Kubaschewski(30). Above 0·7% manganese in the iron the inclusions were almost pure MnO. The results are of little value in showing the effect of manganese on the solubility of oxygen in liquid iron.

In all the work carried out on the manganese equilibrium it has been assumed that manganese has no effect on the activity coefficient of oxygen in iron. Richardson(31) has suggested from the effects of vanadium and chromium on the activity coefficient of oxygen in iron (fo) that 0·5% manganese might lower it to 0·9 and 1% Mn lower it to 0·8.

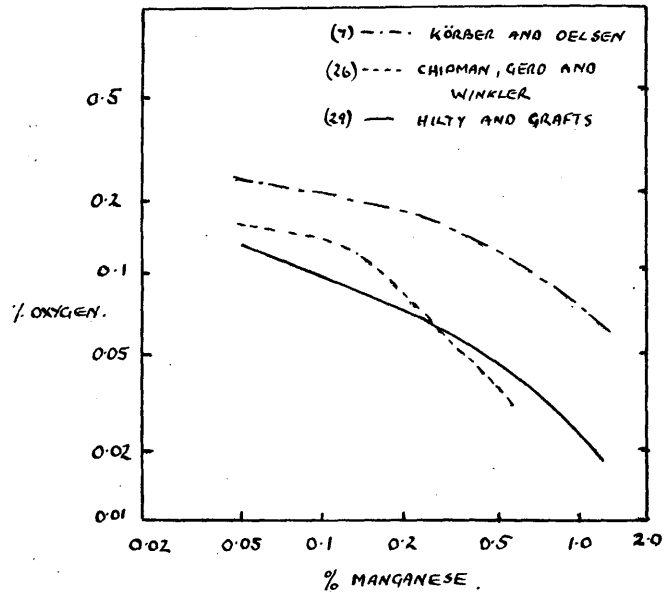


FIG 3. MANGANESE - OXYGEN EQUILIBRIUM IN LIQUID IRON AT 1550 °C.

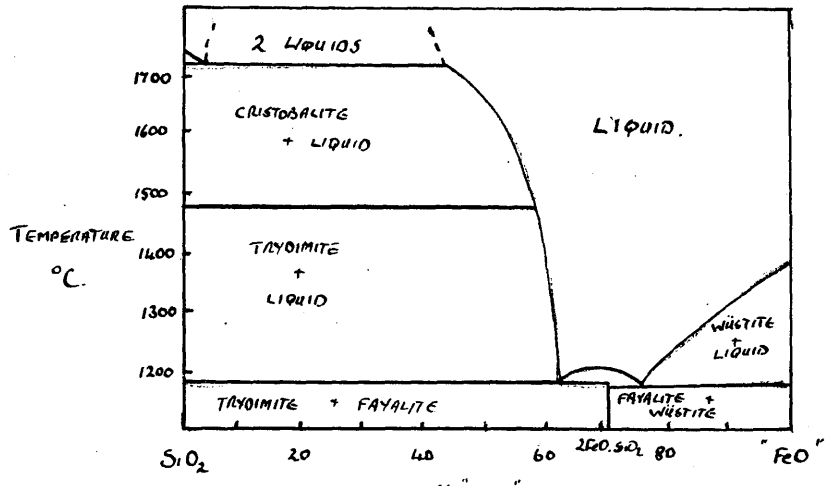


FIG. 4 "FeO" - SiO_2 SYSTEM (32)

Manganese is intermediate between chromium and vanadium in affinity for oxygen and 1% vanadium reduces fo to 0·52 while 1% chromium reduces it to 0·9. In the range of manganese contents in which the work on the manganese equilibrium has been carried out this effect will be very small and within the experimental errors involved. When a deoxidising element reduces fo its effect on the oxygen concentration of the melt is not as great as would be expected from affinity considerations.

3. Ferrous Oxide - Silica system.

The approximate phase diagram for this system is shown in Fig.4; it shows that ferrous oxide and silica are not completely miscible in either the liquid or solid state. In the liquid state there is a region of immiscibility typical of most systems between silica and a basic oxide while in the solid state a compound $2FeO.SiO_2$ (fayalite) exists. The existence of the zone of immiscibility in the liquid state suggests that there might be a positive deviation from ideality in the activity of ferrous oxide in $FeO-SiO_2$ slags and the existence of the compound fayalite indicates a tendency for a negative deviation. These opposing factors suggest that ferrous oxide should not behave ideally in these slags but that the deviations from ideality should not be as great as would be the case if only one factor was involved.

Some data obtained by Taylor and Chipman(13) on the oxygen partition between liquid iron and $FeO-SiO_2$ slags indicated that ferrous oxide behaved ideally in these slags up to silica saturation. A more extensive and precise measurement of ^{a}FeO in $FeO-SiO_2$ slags has been made by

Schuhmann and Ensio(33) who studied the equilibrium between these slags, γ-iron and a CO/CO_2 gas mixture. From this study they found the activity of ferrous oxide in these slags; their results are used for the binary $FeO-SiO_2$ part of Fig.15. This indicates a slight positive deviation from ideality with silica contents up to 25 mol. per cent and a negative deviation above this which increases with silica content up to silica saturation. At silica saturation Schuhmann and Ensio found the a_{FeO} to be

$$\log a_{FeO} = \frac{300}{T} - 0{\cdot}590$$

in contact with γ-iron. If this is extrapolated to the melting point of iron it indicates a_{FeO} of 0·377 at this temperature, the concentration of ferrous oxide being 0·48 mol.fraction.

4. Silicon-oxygen equilibrium in liquid iron.

When silicon is added to liquid iron containing oxygen the equilibrium is

$$[Si] + 2[O] = (SiO_2) \qquad K = \frac{(a_{SiO_2})}{[a_{Si}]x[a_o]^2}$$

The activity of silica can be affected by combination with ferrous oxide but virtually all experimental work carried out on this equilibrium has been performed using silica crucibles. This fixes the activity of silica as unity and the deoxidation constant reduces to

$$K = \frac{1}{[a_{Si}]x[a_o]^2} \quad \text{or} \quad K_{Si} = [a_o]^2 \times [a_{Si}]$$

Two experimental methods have been used in studying this equilibrium, the gas-metal and slag-metal methods. Zapffe and Sims(34) and Chipman and Gohcen(35) have used the gas-metal approach. In this method a mixture of hydrogen and water vapour was used to control the oxygen potential of the gas and the molten iron held in a silica crucible was brought to equilibrium with this gas.

Zapffe and Sims carried out an investigation of the reaction

$$2H_2O + [Si] = 2H_2 + SiO_2(\text{solid})$$

$$K = \left(\frac{p_{H_2}}{p_{H_2O}}\right)^2 \frac{1}{[Si]}$$

but did not carry out any extensive investigation of the oxygen contents of the metal. The oxygen determinations which Zapffe and Sims did make indicated that silicon affected the activity coefficient of oxygen in iron, which they explained as being due to the presence of silicon monoxide in the melt reducing the effective concentration of oxygen, in terms of the structure of the melt one atom of oxygen would tend to be associated with one atom of silicon.

The work of Zapffe and Sims has been repeated by Chipman and Gokcen using a more refined experimental technique in which steps were taken to prevent errors due to thermal diffusion and also a study was made of the rate of approach to equilibrium. It is interesting to note that the controlling reaction was the one between the gas and metal and that the crucible and metal were always in equilibrium with each other. The equilibria involved were

$$(SiO_2) = [Si] \quad 2[O] \qquad K_1' = [\%Si]\,[\%O]^2$$

$$(SiO_2) + 2H_2 = [Si] + H_2 \qquad K_2' = [\%Si]\left\{\frac{h_{H_2O}}{h_{H_2}}\right\}^2$$

On plotting the oxygen content of the metal against the ratio H_2O/H_2 with which it was in equilibrium a ratio was reached at which the oxygen content of the metal remained constant with increasing values of H_2O/H_2. This oxygen content was the concentration at which a silica saturated $FeO\text{-}SiO_2$ slag was formed and was the concentration in equilibrium with this slag. At 1600°C the concentration was 0·088% giving a value of $\frac{0\cdot088}{0\cdot225} = 0\cdot39$ for the activity of ferrous oxide in this silica saturated $FeO\text{-}SiO_2$ slag, 0·225% being the oxygen saturation value at 1600°C. This value agrees reasonably well with the figure of 0·377 obtained by extrapolating the results of Schuhmann and Ensid (33) to 1527°C., the melting point of iron.

Fischer and vom Ende(14) using silica crucibles and high frequency heating have studied the effect of temperature on the oxygen content of liquid iron in equilibrium with silica-saturated $FeO\text{-}SiO_2$ slags. The rather high ferric oxide contents of their slags was probably due to the air atmosphere used. From Fischer and vom Ende's results the activity of ferrous oxide is shown in Table 2.

Table 2.

Temperature	1550°C	1600°C	1650°C	1700°C
a_{FeO}	0·43	0·42	0·39	0·37
Mol. fraction FeO (32) at saturation.	0·48	0·47	0·43	0·37
% FeO	0·9	0·9	0·91	1·0

These data indicate that the activity of ferrous oxide in a silica-saturated $FeO-SiO_2$ slag falls with increasing temperature, a trend which was in conflict with the work of Schuhmann and Ensio who found that a_{FeO} increased with increasing temperature in silica saturated $FeO-SiO_2$ slags. Rey(36) has also shown from the heat of solution curve for FeO in $FeO-SiO_2$ slags that a_{FeO} should increase with increasing temperature. But it should be noted as shown in Table 2 that in Fischer and vom Ende's work the activity coefficient of ferrous oxide (γ_{FeO}) increased with increasing temperature due to the fact that the concentration of FeO in silica saturated $FeO-SiO_2$ slags decreases as the temperature rises. Thus the results of Fischer and vom Ende are not in conflict with Rey and Schuhmann and Ensio, as has been suggested by Turkdogan and Pearson(37).

For the equilibrium

$$SiO_{2(CRIST.)} = [Si]_{Fe} + 2[O]_{Fe}$$

Chipman and Gokcen(35a) have given the following values

$$\Delta G^{o} = 133{,}340 - 50{\cdot}37T$$

$$\log k_1 = \frac{-29{,}150}{T} + 11{\cdot}01 \quad \text{where} \quad k_1 = [a_{Si}][a_{O}]^2$$

Their data on the equilibrium was summed up in the ternary system Fe-O-Si shown in Fig.5.

Körber and Oelsen(38) have studied this equilibrium using silica crucibles and heating in a carbon tube resistance furnace in an atmosphere of nitrogen. Temperature measurements were made by an optical pyrometer checked occasionally by immersion readings with a platinum-platinum rhodium thermocouple. The slags used were $FeO-MnO-SiO_2$ slags with a small quantity of alumina picked up from the crucible. From a large number of melts Körber and Oelsen(38) obtained a value for the equilibrium

$$Si + 2FeO = SiO_2 + 2Fe \qquad k = \frac{[a_{Fe}]^2 (a_{SiO_2})}{(a_{FeO})^2 [a_{Si}]}$$

Since the activity of iron was approximately constant and the activity of silica was unity this reduces to

$$K = (a_{FeO})^2 [a_{Si}]$$

or using weight concentrations $K = (\%FeO)^2 [\%Si]$

Körber and Oelsen found K to be independent of the relative amounts of FeO and MnO in the slag and also of the composition of the metal and reported its value as

$$\log K = \frac{-19,057}{T} + 11.1008 \quad \text{where} \quad K = (\%FeO)^2[\%Si]$$

giving $K = 4.5$ at 1550°C.

Since Körber and Oelsen determined the oxygen content of their melts, this can be substituted for (FeO) in the expression for K giving

$$K_{Si} = [\%O]^2[\%Si] = 1.34 \times 10^{-5} \text{ at } 1550°C.$$

This result compares with the value of 1.1×10^{-5} obtained by Chipman and Gokcen and 1.6×10^{-5} obtained by Hilty and Crafts(29).

The figure obtained by Hilty and Crafts was from experiments carried out in a rotating crucible furnace using silica, magnesia and alumina crucibles. Owing to the difficulties already mentioned only metal data were obtained and the results were plotted as a relation between the oxygen and silicon contents of the metal. This indicated that the different crucible materials had no significant effect on the equilibrium except at very low silicon contents. This was surprising since it might have been expected that magnesia and alumina would increase the deoxidising power of silicon by reducing the activity of silica because of the tendency to silicate formation.

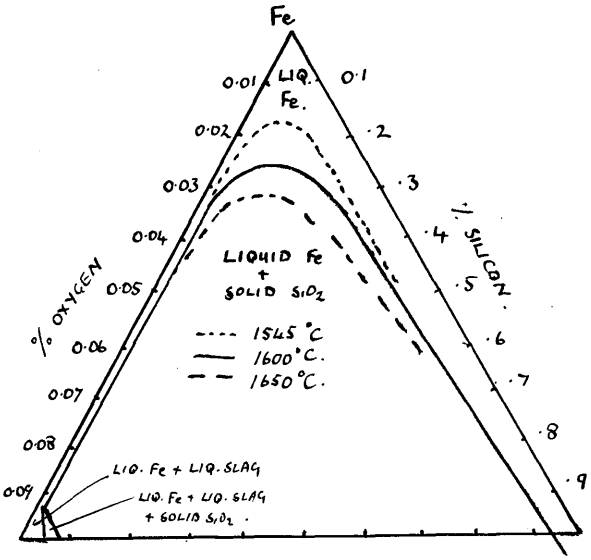


FIG. 5 ISOTHERMAL SECTION OF Fe-O-Si SYSTEM AT 1545, 1600, 1650 °C (CHIPMAN AND GOKCEN)[35]

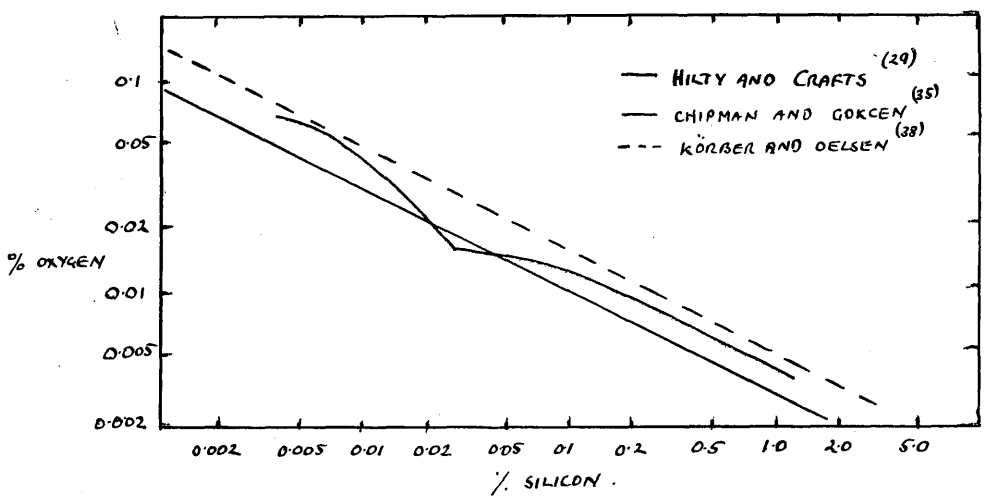


FIG. 6 SILICON – OXYGEN EQUILIBRIUM IN LIQUID IRON 1550°C.

Hilty and Crafts plotted the relation between silicon and oxygen as two intersecting curves (Fig.6). It was suggested that this intersection marked the change from equilibrium with a liquid silicate to equilibrium with solid silica, i.e., was the point of three phase equilibria, solid silica, liquid silicate and liquid iron. Darken(39) has pointed out that the gradient of the curves at the join violates the laws of heterogeneous equilibria as their metastable extensions pass into the homogeneous phase field, i.e., liquid iron. Hilty and Crafts results indicate that the oxygen content of iron in equilibrium with a silica saturated $FeO-SiO_2$ slag is 0·04% at 1600°C, i.e., the value at the point of three phase equilibrium. This is much lower than the figure of 0·088% oxygen obtained by Chipman and Gokcen for the same equilibrium. The results of Körber and Oelsen(38), Hilty and Crafts(29) and Chipman and Gokcen(35) for the silica oxygen equilibrium are compared in Fig.6.

Using a similar technique to that already discussed for their work on the deoxidation of iron by manganese, Evans and Sloman(40) have studied deoxidation by silicon. The total oxygen content of their melts for any given silicon content was much higher than that expected from Chipman and Gokcen's results at 1527°C; this was probably the result of incomplete removal of the deoxidation product, silica, from the iron. This work gave little information on the silicon-oxygen equilibrium in liquid iron but may be useful in showing the composition of the deoxidation products formed when iron is deoxidised by silicon. The results showed that at silicon contents above 1% the inclusions consisted of almost pure silica.

5. Oxygen Equilibrium between molten iron, manganese and silicon.

All the experimental data on this equilibrium has been obtained from slag-metal experiments. Körber and Oelsen(38) have studied the equilibrium under silica saturated FeO-MnO-SiO_2 slags, their technique having already been mentioned. They determined K'_{Mn} for a wide range of FeO and MnO contents and found it to be independent of the ratio $\frac{(FeO)}{(MnO)}$, within the limits of experimental error. K'_{Mn} was found to be considerably higher in these slags than with simple FeO-MnO slags; Körber and Oelsen reported it as

$$\log K'_{Mn} = \frac{7940}{T} - 3{\cdot}172$$

giving a value of 15·5 at 1550°C, compared with 3·8(26) and 2·4(7) found for FeO-MnO slags. The data of Körber and Oelsen on this equilibrium show a large scatter and if plotted on a statistical basis as in Fig.7, values of 13 to 18 for K'_{Mn} occur with almost equal frequency indicating a value of K'_{Mn} of 15·5 $\pm$ 2·5.

The oxygen determinations made by Körber and Oelsen showed that the ratio $\frac{[\%O]}{(FeO)}$ was independent of the $\frac{(FeO)}{(MnO)}$ ratio of the slag and was 0·17 at 1550°C.

Krings and Schackmann(41) have made a study of the effect of silica on K'_{Mn} in slags which were not silica saturated. This work was carried out using alumina crucibles giving slags which contained up to 26% alumina. No determinations were made of the oxygen content of the melts. The results for K'_{Mn} showed that the value increased with increasing silica content in the slag and at a mole fraction silica of 0·5 it was 10·8. Krings and Schackmann's results are shown in Figs. 12 and 13.

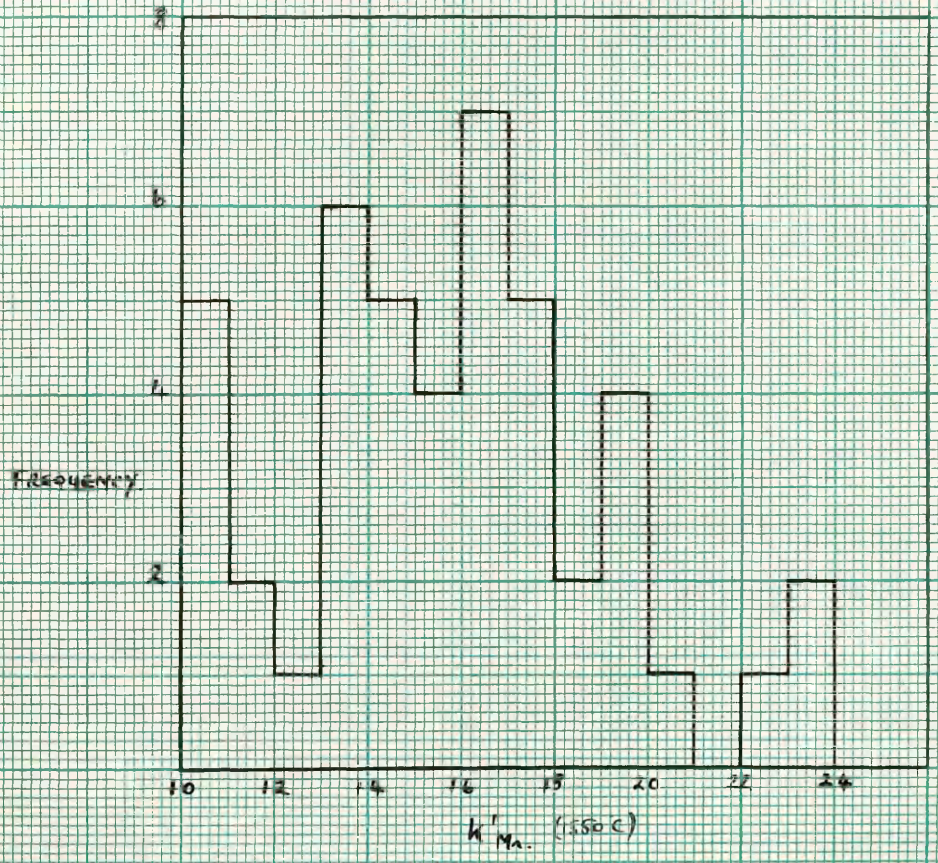


FIG 1. STATISTICAL EXAMINATION OF KOITRER AND OELSEN[18]

RESULTS ON k'_{Mn} IN SILICA SATURATED SLAGS

Körber and Oelsen obtained data on the manganese-silicon equilibrium in liquid iron, which can be represented by the equation:-

$$Si + 2MnO = SiO_2 + 2Mn \quad K_T = \frac{[a_{Mn}]^2 x (a_{SiO_2})}{[a_{Si}] x (a_{MnO})^2}$$

Using weight concentrations in place of activities and putting a_{SiO_2} equal to unity as the slags were silica-saturated, the equilibrium becomes

$$K'_{MnSi} = \frac{[Mn]^2}{(MnO)^2[Si]}$$

Körber and Oelsen found this to be represented by the equation

$$(\log K'_{MnSi}) = \frac{+3177}{T} - 4.757$$

giving a value of 9.6×10^{-4} at 1550°C.

When manganese is used in conjunction with silicon it is a much more effective deoxidiser than when used alone. This is shown by Fig.8, where a comparison is made between the effect of manganese on the oxygen content of molten iron in the presence and absence of silicon. This indicates that with 1% manganese the oxygen concentration in the presence of silicon is only 1/9th of that in its absence.

Hilty and Crafts(29) have carried out work on the relation between manganese, silicon and oxygen in molten iron, using alumina and magnesia crucibles in the rotating furnace. Their results were plotted from the data obtained using alumina crucibles and on the basis of the composition of the metal since the slag data was unreliable. The oxygen contents for corresponding silicon contents were higher in the melts made in magnesia crucibles. This may have been due to either alumina lowering γ_{FeO} in $FeO-MnO-SiO_2$ slags or to magnesia raising it. This effect was most marked in melts with low silicon contents; in these melts the FeO content of the

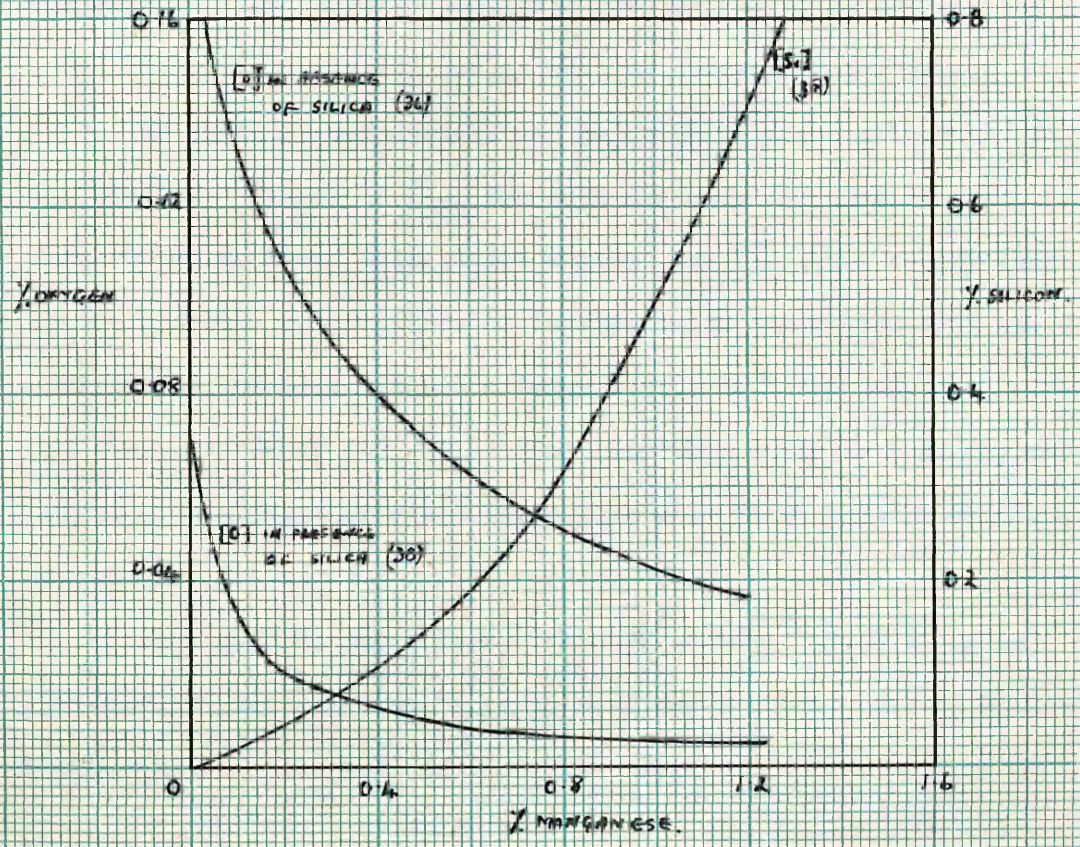


FIG 8 EFFECT OF MANGANESE ON THE OXYGEN CONTENT OF IRON AT 1550°C

slags was highest and the alumina pick up was therefore greatest, whereas the magnesia pick up was least in these slags.

In their graphs showing the effect of silicon on the oxygen content of the metal containing different concentrations of manganese, a similar inflexion to that already mentioned for their work on the silicon-oxygen equilibrium was indicated and is open to the same objections.

No reliable conclusions can be drawn from the slag data of Hilty and Crafts. Values of K'_{Mn} for both magnesia and alumina crucible data showed no trend with silica content and there was a very large scatter in the results. Activities of ferrous oxide calculated from the oxygen contents of the melts showed a large scatter and the only factor noticeable was a tendency for γ_{FeO} to be less than unity, a tendency more marked with alumina crucible melts than with those made in magnesia crucibles.

Some data on the effect of silica on K'_{Mn} and on γ_{FeO} in $FeO-MnO-MgO-SiO_2$ slags can also be obtained from the work of Winkler and Chipman(28). This will be discussed later.

(6) Slag-Metal Equilibria.

Several methods have been used in an attempt to interpret slag-metal equilibria in terms of the Law of Mass Action. It was soon realised that the use of molar concentrations for slag components as determined by chemical analysis rarely gave constant equilibrium constants. Slags could not therefore be regarded as ideal solutions. Various hypothesis have been advanced to explain the deviations from ideality. The first to achieve prominence was that in which certain compounds were assumed to

exist in the slag. Activities were then equated to the uncombined or "free" oxides present. Schenck(42) in particular has used this method extensively to interpret the various slag-metal equilibria. Thus in molten iron silicates

$$(\Sigma FeO) = (FeO) + 0{\cdot}7\ (2FeO.SiO_2)$$

where (ΣFeO) = total ferrous oxide

(FeO) = "free" FeO

$(2FeO.SiO_2)$ = concentration of fayalite in the liquid silicate.

The "free" FeO content can therefore be calculated if the "dissociation constant" of fayalite:-

$$D_{FeS} = \frac{(FeO)^2\ (SiO_2)}{(2FeO.SiO_2)}$$

is known. By using the concept of free concentrations, which is similar to the concept of activity in the modern thermodynamic approach, Schenck has constructed diagrams showing "free" ferrous oxide contents in slag systems at various temperatures. Thus Fig.9, which shows the "free" ferrous oxide contents in $FeO-MnO-SiO_2$ slags, indicates that the "free" ferrous oxide contents are lower than the total ferrous oxide contents, i.e., the activity coefficient is lowered in the presence of MnO and SiO_2. Further diagrams were constructed by Schenck showing the manganese, silicon and oxygen contents of iron in equilibrium with $FeO-MnO-SiO_2$ slags.

White(43) has used a similar approach, which was applied by Murray and White(44) to the equilibrium between liquid iron and $FeO-MnO-SiO_2$ slags at 1600°C assuming that the compounds $FeO.SiO_2$, $2FeO.SiO_2$ and $MnO.SiO_2$ exist in the slag. Calculations were made of the effect of silica on K'_{Mn} taking the value of K_{Mn} obtained by Körber and Oelsen in

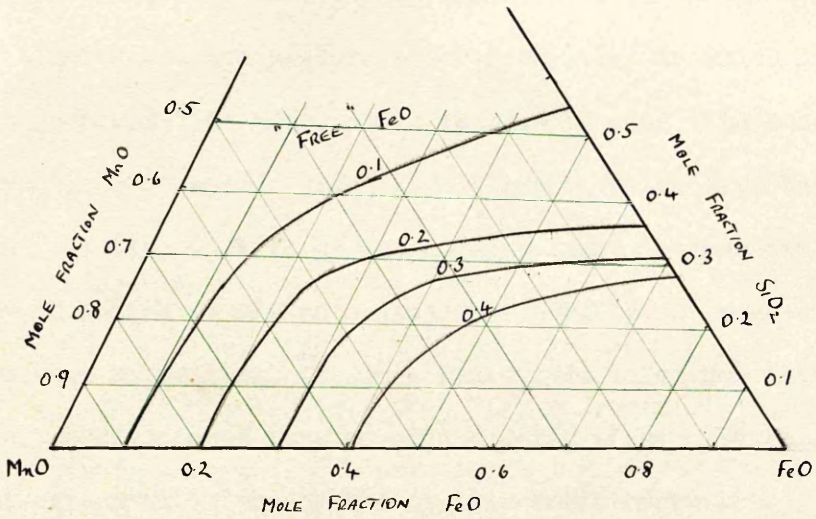


FIG 9. "FREE" FeO CONCENTRATIONS IN SYSTEM FeO - MnO - SiO_2 AT 1577 °C. (SCHENCK (40))

simple oxide slags as the true value. Their calculations showed that K'_{Mn} increased with increasing silica content up to silica saturation.

Although the concept of the existence of compounds in liquid slags is somewhat formal and can hardly be regarded as an exact picture of their constitution - as was pointed out by Murray and White - it is useful in predicting the effect of one slag constituent on the activity of another.

A more accurate picture is probably that in which liquid slags are assumed to consist of ions, since this is in line with modern views on the structures of solid oxides and silicates which have been shown by X-ray diffraction work to be essentially ionic in character. As the low entropy of fusion of silicates suggests that there is no radical change in structure on melting, it seems reasonable to assume that the liquid slag is merely a disordered version of the solid slag. There is, however, some disagreement on the nature of this ionic structure. Thus, Herasymenko(45) assumed that the cations and anions were randomly distributed in the melt and took up positions regardless of sign or charge, whereas Temkin(46) postulated that the cation positions were filled by cations only but quite randomly and irrespective of charge, the anion positions being similarly occupied by anions. Herasymenko's concept is similar to that of a gas in which the thermal movement of the ions overcome the electrostatic attractive forces between oppositely charged ions. Thus if Σn_m is the total number of cations and Σn_x of anions, then the ionic fraction on the Herasymenko model is

$$N_{M^+} = \frac{n_{M^+}}{\Sigma n_M + \Sigma n_X}$$

On the Temkin model the structure of the slag is determined to a large extent by electrostatic forces, and the ionic fraction is given by

$$N_{M^+} = \frac{n_{M^+}}{\Sigma n_{M^+} + \Sigma n_{M^{++}} + \Sigma n_{M^{3+}} + \cdots}$$

Flood, Førland and Grjotheim[47] have pointed out that there is an important difference between Temkin's model and a mixed ionic crystal in that the substitution of a monovalent ion by a divalent one requires the creation of a vacant cation position, hence a divalent cation is equivalent to an adjacent pair of monovalent cations. Flood therefore defines the ionic fraction by

$$N_{M^{++}} = \frac{2\, n_{M^{++}}}{n_{M^+} + 2\, n_{M^{++}} + \cdots}$$

since this represents the solid structure of the crystal better. These ionic fractions are used instead of concentrations in expressions for equilibrium constants. In the above approaches to slag-metal equilibria assumptions must be made with regard to the constitution of liquid slags. This is not necessary in the purely thermodynamic approach, in which experimental determination of the activities of slag components and of elements dissolved in liquid iron and their heat and entropies of mixing are made. Various methods have been used to calculate these thermodynamic quantities including studies of gas-slag, gas-metal and slag-metal equilibria. Since a great deal of experimental data on these quantities is not yet available, approximate calculations have been made using phase diagrams notably by Richardson(48), Rey(36) and Chipman(49).

This latter approach in which deviations from ideality are expressed in terms of activity coefficients will be used in the present work.

EXPERIMENTAL TECHNIQUE.

III. EXPERIMENTAL TECHNIQUE.

1. Crucibles.

One of the biggest practical difficulties in slag-metal experiments is obtaining a suitable container which will resist attack by both slag and metal and which will not have a great effect on the equilibrium being studied. The rotating crucible furnace developed by Taylor and Chipman(13) appeared to offer big advantages for slag-metal work when it was first described, but these advantages now appear to be confined to a very limited range of slag composition. It was found by Hilty and Crafts(29) and Murad(50) that using FeO-MnO-SiO_2 slags in this type of furnace it was impossible to keep the slag in the metal cup and that it crept up the walls of the rotating crucible. It has been pointed out (Bell, Murad and Carter(51)) that the height of rise of the rotating liquid is independent of its density and that if surface and interfacial tension effects are excluded the slag must come into contact with the crucible. For the rotating crucible to be successful the slag must have a high contact angle and interfacial tension against molten metal and also the metal must wet the crucible. These conditions do not exist in molten iron and FeO-MnO-SiO_2 slags. It is also probable that even if contact between the slag and crucible were prevented crucible attack could still take place through oxygen in the metal. In this case the metal might tend to come to equilibrium with the crucible rather than with the slag layer which is usually thin with induction heating. The use of induction heating in slag-metal work although giving a certain amount of stirring to the melt has the disadvantage that the slag layer

is not heated directly. Attempts have been made to overcome this draw-back by using a coil of molybdenum strip, heated electrically, held above the slag (Fetters and Chipman(10)) or by an electric arc above the slag (Winkler and Chipman(28)). As in this work it was decided to heat the slag and metal equally, it was necessary to find a crucible which would be impervious to slag and metal at temperatures above the melting point of iron.

A study of the thermal equilibrium diagrams for metallic oxides showed that magnesia appeared the best available crucible material for use with $FeO-MnO-SiO_2$ slags. Magnesia forms solid solutions with both ferrous and manganous oxides and the melting point of these solutions rises rapidly with increasing magnesia content. The magnesia pick up in slag attack by these oxides is therefore not large. The addition of silica to these oxides increases the solubility of magnesia as is indicated by the $FeO-MgO-SiO_2$ ternary system(52)(Fig.10), but with silica contents below 30% the attack is not serious enough to destroy the crucible. The use of magnesia as a crucible material meant that another component was introduced into the slags, but as yet no method has been found of varying the concentrations of three components of a slag in slag-metal experiments without introducing a fourth.

Several methods have been tried to produce magnesia crucibles with a low permeability. Barret and Holbrook(53) attempted to make fused magnesia crucibles by filling a graphite crucible with magnesia powder and heating it by high frequency heating to give a fused layer

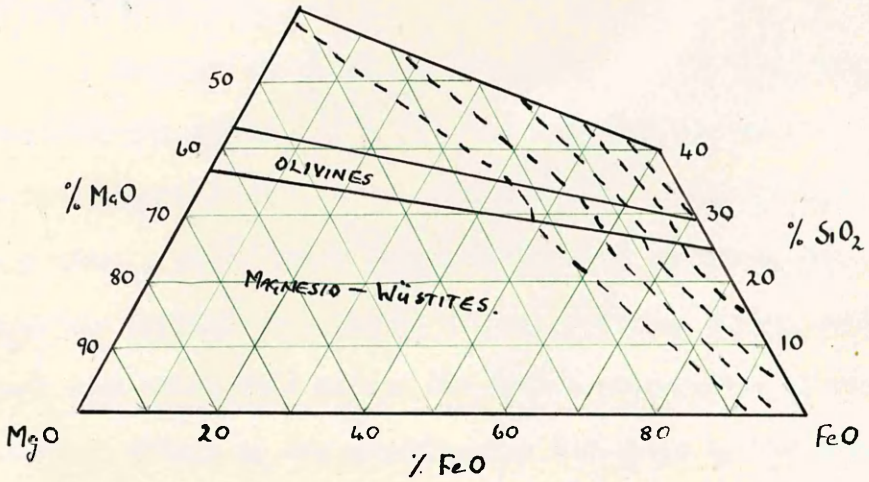


FIG 10 PHASE DIAGRAM $FeO - MgO - SiO_2$ (52)

of magnesia on the internal walls of the graphite. This method was tried and although producing a crucible which would hold molten iron, as soon as a slag was added it soaked into the crucible and would not remain as a layer on top of the metal. These crucibles were therefore unsuitable for slag-metal work.

A similar technique to that of Barret and Holbrook was used by Dancy(54) but instead of a graphite crucible the magnesia powder was packed round a graphite core. This assembly was heated by high frequency current to produce a fused layer of magnesia round the core, the core being removed while the crucible was hot to prevent cracking during cooling. It was found that using this method the fusion temperature of magnesia was easier to attain as the graphite was insulated by the magnesia powder, but considerable reduction of magnesia took place. Although the crucibles produced by this method were found to be an improvement on those of Barret and Holbrook, they had a high permeability and did not resist slag penetration. This finding was confirmed by Dancy(55) when in a paper on the reduction of ferrous oxide by carbon saturated iron it was shown that as soon as ferrous oxide came into contact with the crucible it was destroyed. As these crucibles have only a thin fused layer on the surface of the crucible, when this layer is penetrated the crucible is useless. They will contain molten iron only because of the high contact angle between molten iron and magnesia.

Several proprietary crucibles were tried and although an improvement on the above, they were not sufficiently impermeable to slag.

Efforts were therefore made to produce an impermeable crucible by slip-casting. It had been shown by Thomson and Mallet(56) that any refractory oxide can be made sufficiently plastic to be slip cast by grinding very finely. It was recommended that magnesia be ground for 17 hours to make it suitable for slip casting. It was found in the present work that longer grinding periods gave better results and 24 to 30 hours was used. Due to its tendency to hydrate, magnesia cannot be slip cast using an aqueous slip. Crucibles cast by aqueous slips were riddled with cracks when dried. Some patented methods for producing magnesia crucibles using an aqueous slip exist, but these use added oxide such as B_2O_3 to prevent hydration thus adding further impurities to the crucible.

It was found using ordinary alcohol (containing about 5% water) that it was almost impossible to obtain crucibles which did not crack either on drying or firing. Absolute alcohol was tried as Thomson and Mallet had found that crucibles free from cracks could be produced using this as a slip casting medium. This proved successful in producing crucibles but often up to 50% of the crucibles showed cracks after firing. It was, therefore, decided that complete drying of the alcohol might increase the yield of sound crucibles. The Grignard method of drying alcohol was used and alcohol dried by this method gave very satisfactory results, producing a yield of 95% sound crucibles.

The technique used to make these crucibles was first to grind fused magnesia in a ball mill for about 24 hours. All the crucibles used in this work were made from magnesia ground in a steel ball mill using steel balls. This resulted in a small pick up of iron but did not lead

to any difficulties in the process or in the experimental work. Crucibles have also been produced using magnesia ground in rubber lined ball mill with alumina balls and with only a very small alumina pick up.

The ground magnesia was mixed with dried alcohol, adding the magnesia to the alcohol a little at a time until a slip of the desired consistency had been produced. This usually contained about 50% by volume of powdered magnesia but the quantity was not measured, it being judged by the consistency of the slip. At first the slip was allowed to stand overnight before being used but later it was found that it could be used immediately after mixing.

Good plaster of Paris moulds were found to be essential for the production of magnesia crucibles. These moulds were made using fine plaster of Paris and sprinkling it into water, avoiding lumps and keeping the mixture well stirred until it was of a creamy consistency. The mixture was then poured into a greased mould containing a metal core which was the shape of the crucible desired. Once the plaster had set the metal core and the mould were removed and the plaster mould allowed to air dry for several days. A crucible shape was chosen with a slight taper from top to bottom to make it easier to extract the slip cast crucible from the plaster mould.

The crucibles were made by filling the plaster mould with the alcohol slip and when a sufficient thickness of magnesia had formed round the walls the superfluous slip was poured off. Considerable difficulty was encountered at first in removing the crucibles from the mould since they tended to stick to the plaster and did not shrink away on drying.

It was found that if the plaster mould was dusted with French chalk before casting each crucible, trouble due to sticking was obviated. In some experiments on the effect of grinding time it was found that longer grinding reduced the tendency for sticking in the mould, and only an occasional dusting with French chalk was necessary if the magnesia was ground for 30 hours. An almost limitless number of crucibles could be produced from one plaster mould since the alcohol slip had no effect on the plaster.

The crucibles were dried for about 24 hours before being fired, and in the dried state were fragile although some shaping could be done on them if carried out carefully. The crucibles were fired in a gas fired muffle to about 1600°C, the temperature being raised slowly and the crucibles being allowed to cool in the furnace.

After firing the crucibles were mechanically strong and almost impervious to gases. Their main drawback was a low spalling resistance which rendered them unsuitable for high frequency heating.

Two types of crucible were produced, one using fused magnesia which contained approximately 3% silica, the other using a high purity fused magnesia containing about 0·3% silica. On firing the first type had a polished surface showing some slight fusion of the bond at 1600°C whereas the purer magnesia crucibles had a matte surface after firing. Both types of crucible were impervious after firing. The purer magnesia crucibles were used when it was necessary to keep the silica content of the slags as low as possible.

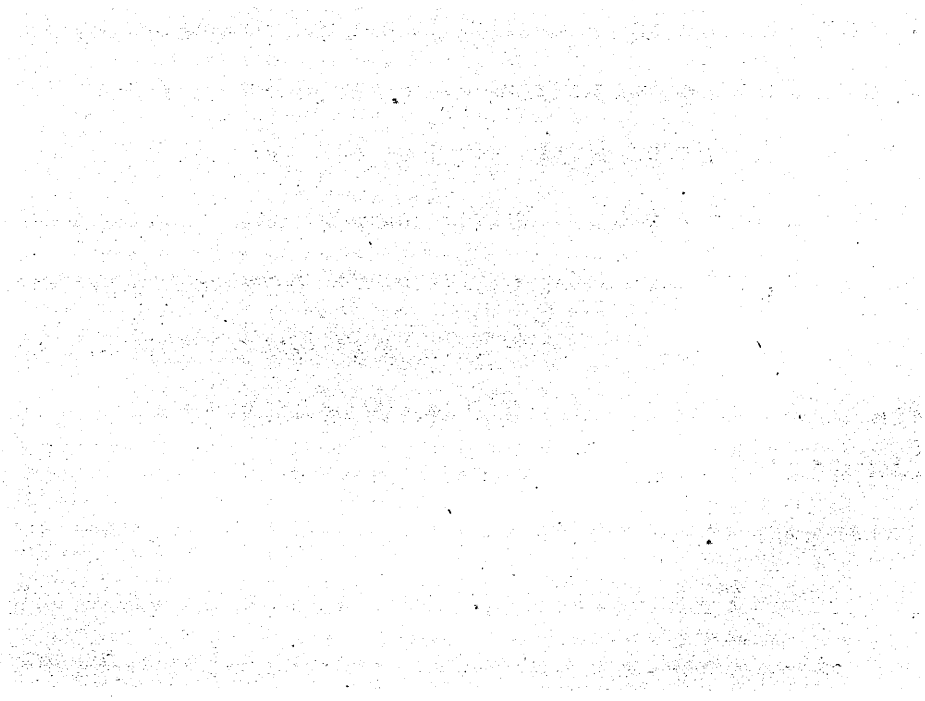
Using slip-cast magnesia crucibles, molten iron could be maintained in contact with an FeO-MnO-SiO_2 slag for an almost unlimited time at 1550°C.

The slag picked up magnesia by attack on the surface of the crucible but did not penetrate it. This pick-up of magnesia depended mainly on the silica content of the slag, being greater the higher the silica content. There was a slight variation in the amount of magnesia pick-up depending on the FeO/MnO ratio; at any given silica content the pick-up tended to be higher the greater this ratio.

For some melts silica crucibles were required and several types of fused silica crucibles were tried. It was found that the main cause of failure in silica crucibles was due to devitrification of the silica. As long as the slag added contained enough silica to prevent too great an attack on the crucible there was little or no trouble from failure due to slag attack. Devitirification appeared to start at the walls of the crucible and progress inwards so that if a thick walled crucible were used failure due to this cause could be delayed. Using silica crucibles with a wall thickness of 1/4 inch, slag and metal could be held at 1550°C for at least two hours without crucible failure. The silica crucibles used in this work were made from silica tubing $1\frac{1}{2}$ inch external diameter and 1/4 inch wall thickness onto which an end had been fused using silica sheet of the same thickness. These crucibles proved very satisfactory for this work.

To protect the magnesia crucibles from contact with the furnace tube thin slip cast alumina crucibles were used. These crucibles were made by grinding fused alumina for about 12 hours in a ball mill and afterwards treating it with 10% hydrochloric acid. This removed the iron picked up during grinding and gave the necessary acidity for slip

casting alumina. The alumina was allowed to settle in the acid, the excess acid decanted off and the consistency of the slip adjusted with water. The crucibles were then made in plaster moulds, dried and fired at 1600°C. This firing temperature did not give an impermeable crucible but was satisfactory for the purpose required.



11. Materials used in melts.

Metallic charge.

Armco iron from which the scale had been completely removed was used as a source of iron. The main impurities were:-

Carbon	Manganese	Phosphorus	Sulphur	Silicon
0·012%	0·017%	0·005%	0·025%	0·003%

Manganese was added as electrolytic manganese and silicon as lump silicon.

Slag materials.

The silica used to make the slag additions was a natural silica of >99% SiO_2. It was ground and further purified by boiling with concentrated hydrochloric acid to remove any metallic oxide impurities.

Ferrous oxide was prepared from ferrous oxalate by heating in vacuum in an iron tube to 1000°C. After holding for about an hour at this temperature the tube was sealed to hold the vacuum and then quenched in water. This gave ferrous oxide slightly richer in oxygen than the stoichiometric formula FeO.

Manganous oxide was made by heating manganese oxalate up to 1100°C in an atmosphere of cracked ammonia. The gas was continually passed during heating and the material was cooled in the same atmosphere. This method produced manganous oxide of a bright green colour and this was stored in a sealed bottle.

111. Furnace and Apparatus.

The melts were carried out using a platinum wound resistance furnace, as shown in Fig.11. The furnace tube used was a 1½ inch internal diameter mullite tube which could be used up to 1700°C and which was impervious to gases up to this temperature. This tube was placed inside a thin alundum tube on which the platinum wire was wound. The tube was wound over a length of 14 inches with 20 S.W.G. platinum wire and the furnace insulated as shown in the sketch. This gave a furnace which at 1550°C was found to have a hot zone of 2 inches in which the temperature did not vary by ±5°C., and which did not vary by ± 10°C over 3 inches. The input to the furnace was controlled by a 16 ampere Variac which gave very sensitive control of the furnace temperature. With this method of control the furnace could be held at 1550°C ±5°C for long periods with only occasional attention.

It was found that if the magnesia crucibles came into contact with the mullite tube at high temperatures they fluxed with the silica in the mullite and stuck to the tube. To prevent this the magnesia crucible was placed inside a thin alumina crucible. A small depression was made in the base of the alumina crucible into which a fused alumina thermocouple sheath was inserted. The crucibles were supported in the furnace on alundum stools which rested on a rubber bung at the base of the furnace tube, as shown in Fig.11.

The crucibles were located in the furnace so that they were inside the hot zone, as also was the thermocouple tip. The magnesia crucibles were 1½ inches high, thus they could sit completely in the

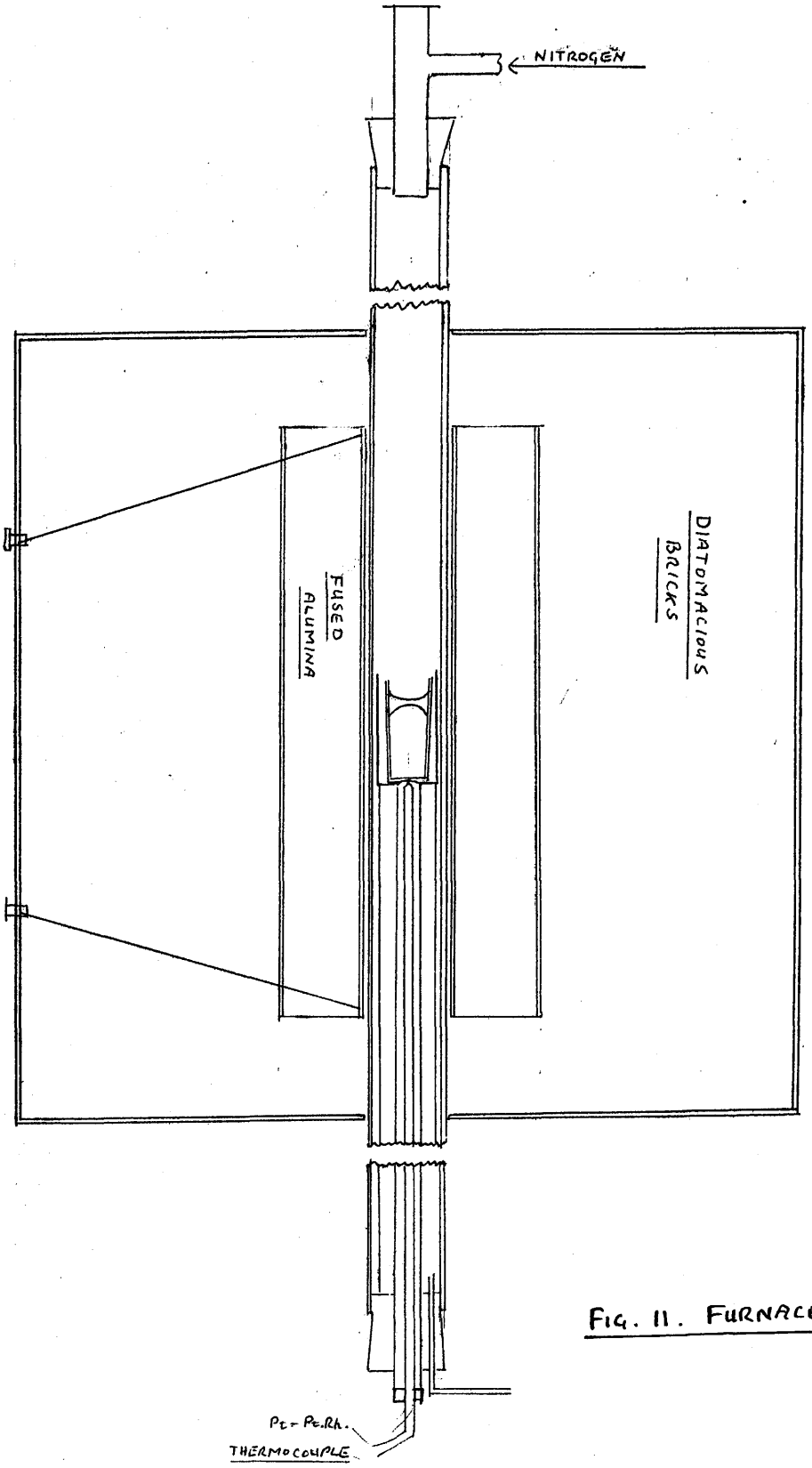


FIG. 11. FURNACE.

hot zone leaving 1/2 inch into which the thermocouple sheath could project. The accuracy of this method of measuring the furnace temperature was checked by suspending a thermocouple inside the crucible and comparing it with the sheathed couple. This showed that the method of temperature measurement was reliable as there was almost no difference in reading between the two thermocouples. Platinum -13% rhodium-platinum thermocouples which had been calibrated against the melting points of gold (1063°C) and palladium (1554°C) were used. The E.M.F. generated by these couples was measured on a Tinsley vernier potentiometer.

Using this method of heating both the slag and metal could be heated directly to the same temperature. As the mullite tube was approximately 36 inches long both ends were cold enough to hold rubber bungs without water cooling. The bung at the top of the furnace held a T-tube with a window and a nitrogen inlet as shown in Fig.11. The nitrogen used was commercial cylinder nitrogen which was purified by passing through a furnace containing four tubes connected in series, the nitrogen passing in succession over copper gauze, steel wool and magnesium turnings held at 600°C. The nitrogen was then dried and passed into the furnace, the gas pressure being maintained at about 1 inch of water above atmospheric pressure.

IV. Experimental Method.

In carrying out a melt a magnesia crucible was first charged with approximately 60 grams of Armco iron, in some cases with the addition of manganese or silicon. The crucible was placed in the furnace as in Fig.11. The nitrogen supply was then connected to the furnace and heating commenced, taking approximately 5 hours to reach 1550°C. The power input to the furnace was controlled so that the rise from 1450 to 1550°C took about one hour, the last 20°C requiring about 20 minutes. This slow method of heating the furnace was adopted to ensure that the platinum winding of the furnace was only slightly above the temperature measured by the thermocouple; this increased the life of the furnace and gave a more accurate control of furnace temperature. A check was obtained on the thermocouple by noting the temperature at which the iron began to melt. Once the furnace temperature had been stabilised at 1550°C the slag was added as a pelleted mixture of ferrous oxide, manganous oxide and silica. In the melts made in magnesia crucibles it was found that 10 grams of slag was sufficient to cover the molten iron. By making the slag addition after the iron was molten it was found that the magnesia pick up was not as great as when the oxides were charged with the metal at the beginning of the melt. This was probably related to the time and area of contact of the molten slag and crucible.

The work of Körber and Oelsen(38), Winkler and Chipman(28) and Krings and Schackmann(41) has shown that equilibrium between iron and $FeO-MnO-SiO_2$ slags is reached rapidly, less than 30 minutes being required. In this work the slag and metal were normally held at 1550°C for approximately one hour before sampling. To establish that equilibrium was

being attained in this time melts were carried out in which equilibrium was approached from different directions, by transfer of manganese from metal to slag and vice versa. Melts were also carried out in which slag and metal, which were in equilibrium according to previous data were used. These were held at 1550°C for 2 hours and sampled. Both methods indicated that equilibrium was attained in less than one hour.

After holding for one hour at 1550°C the slag and metal were sampled. Slag samples were taken by dipping an iron bar into the molten slag to give a chilled layer of slag on the bar. In most melts the iron was sampled by suction into a silica tube using a rubber bulb. For some melts the metal samples were taken using the Carney, Chipman and Grant(57) modification of the Taylor(13) sampler in which the metal is sucked through a short piece of silica tube into a copper block, but this sampler gave trouble at the silica-copper joint and it was found that using silica tube alone identical results were obtained for silicon, manganese and oxygen. The ends of the metal sample were discarded, the centre only being used for analysis. The slag sample was ground and any entrapped iron separated with a magnet.

When the magnesia crucible was removed from the furnace and sectioned lengthwise the slag and metal layers appeared as in Fig.11. It appears that in the presence of a FeO-MnO-MgO-SiO_2 slag that molten iron has a high contact angle with magnesia whereas the slag has a low contact angle. This was one of the main reasons why the rotating crucible furnace was not successful with these slags.

Numerous melts were made using this technique with varying proportions of ferrous oxide, manganous oxide and silica. The magnesia crucibles resisted the attack of these slags without failure with silica contents up to 40%, although when the silica in the slag was above 30% the magnesia pick up increased rapidly with increasing silica.

Some melts were made in silica crucibles to obtain results with silica-saturated slags. Using these crucibles the technique was slightly different from that used with magnesia crucibles. 120 grams of Armco iron were melted in the silica crucible and the temperature stabilised at 1550°C. A slag of ferrous oxide, manganous oxide and silica was added as before using 20 grams with a silica content of about 45% to prevent too large an attack on the crucible. The remainder of the silica necessary to saturate the slag was picked up from the crucible. After 45 minutes at 1550°C the slag and metal were sampled as before. A small quantity of ferrous oxide was then added to the slag to change its composition and the melt held for a further 30 minutes when slag and metal samples were again taken. The slag composition was again altered by adding ferrous oxide and the same procedure repeated. This technique allowed three samples to be taken from one silica crucible.

The contact angle relationships between slag, metal and crucible were similar to those found in magnesia crucibles. Although the crucible was not completely devitrified after 2 hours at 1550°C the surface of the crucible in contact with the slag and metal was devitrified and probably converted to cristobalite, since at 1550°C this is the decomposition product of vitreous silica.

V. Analysis of Slag and Metal.

Slag.

The slag sample was analysed for total iron (ΣFe), manganous oxide, ferrous oxide, magnesia and silica. A sample of the slag was boiled with water and hydrochloric acid added till it was dissolved. The solution was boiled to dryness and baked. The residue was boiled with hydrochloric acid and the silica filtered off and determined by ignition and purification by hydrofluric and sulphuric acids. The iron was determined in part of the filtrate by reduction with stannous chloride and titration with potassium dichromate solution. In the remainder of the filtrate iron and manganese were removed using a basic acetate separation and precipitation in ammoniacal solution by ammonium persulphate respectively. Magnesia was then determined by precipitation with ammonium phosphate and ignition to magnesium pyrophosphate.

The manganous oxide content of the slag was determined by solution in dilute nitric acid using a few drops of hydrofluoric acid to aid solution. The solution was oxidised by sodium bismuthate to give permanganic acid and the manganese determined by titration with ferrous ammonium sulphate and potassium permanganate solutions. The ferrous oxide was estimated by solution in hydrochloric acid in a carbon dioxide atmosphere and titrated with potassium dichromate solution.

In all estimations the weight of sample used was varied according to the expected analytical content.

Metal.

Manganese, silicon and oxygen were estimated in the metal samples. One of two methods was used for manganese depending on the amount present. With contents below 0·5% an absorptiometric method was used while for manganese contents above 0·5% the bismuthate oxidation method was used. Details of both these methods are published in Analysis of Steel and Ferro Alloys(58).

The silicon contents met with in this work were very low and this necessitated a colorimetric method of estimation. Although the molybdenum blue reaction is very sensitive for silicon, reproducible results are very difficult to obtain at low silicon contents. Several methods using the molybdenum blue reaction were tried, mainly differing in the reducing agents used but the only method which gave reproducible results was the method published by the Methods of Analysis Committee of the Iron and Steel Institute(59). This method had modifications for low silicon contents and claimed an accuracy of ±0·002% with silicon contents less than 0·01%. Using this method it was found that the blank steadily increased through each estimation and this trouble was traced to the potassium permanganate solution used. It was found that if a potassium permanganate solution which had been kept in a glass bottle for some time was used the blank was too high to be measured in an absorptiometer, whereas if a new solution of potassium permanganate was used the blank was very low. When this solution was made up and kept in a wax bottle no difficulty was experienced with varying blanks. It was found by this method that silicon estimations could be reproduced to within ±0·001%.

The iron was analysed for oxygen using the vacuum fusion method which is the standard method for determining oxygen in steel. The apparatus used was identical with that described by Murad(50) and the procedure used was in almost all respects the same. The apparatus was first of all degassed by heating the graphite crucible to 2000°C in vacuum. This temperature was maintained for 4 hours when the pressure in the furnace taube was usually of the order of 10^{-4} millimetres mercury. The furnace temperature was then dropped to 1550°C which brought the pressure down to 10^{-5} millimetres mercury. The gas being pumped from the furnace tube in 30 minutes was then collected to give a blank for the apparatus. The apparatus was then ready to receive a metal sample.

The weight of the samples used depended on the probable oxygen content of the metal, and was adjusted so that all the gas produced would be evolved and collected in 15 minutes. These conditions were evolved to suit the particular apparatus and not to overload the diffusion pump which did not work efficiently if the backing pressure rose above 1 millimetre. The backing pressure was kept as low as possible by operating the Toepler pump used to collect the gas samples.

The gas collected was analysed in an Ambler gas analysis apparatus. Carbon dioxide was estimated by absorption in potassium hydroxide solution, oxygen by absorption in alkaline pyrogallol and carbon monoxide using ammoniacal cuprous chloride solution. The nitrogen could be extimated by difference. In almost all cases only carbon monoxide and nitrogen were detected.

The blank was normally of the order of 0·1 to 0·2 c.c. of gas in 30 minutes and contained about 30% carbon monoxide. Thus in 15 minutes the amount of carbon monoxide from the blank was of the order of 0·04 c.c. which was a very small fraction of the carbon monoxide evolved from the metal samples.

The apparatus was checked occasionally by employing samples already analysed at the National Physical Laboratory. For a sample containing 0·02% oxygen the results always agreed within ±0·0005% of this value. No standard samples were available containing higher oxygen contents but in the melts analysed duplicate analysis for oxygen contents above 0·10% did not vary more than ±0·005%. A melt made using only ferrous oxide as a slag addition gave an oxygen content of 0·196% which is comparable with the oxygen saturation figure at 1550°C given by Chipman and his co-workers(10(13).

DISCUSSION OF EXPERIMENTAL RESULTS.

IV. DISCUSSION OF EXPERIMENTAL RESULTS.

1. Experimental Results.

The complete analysis of all the melts made are shown in Table 3. The iron content of the slag has been expressed both as total ferrous oxide (ΣFeO) and as ferrous and ferric oxide. The ferric oxide contents may be rather higher than the actual ferric oxide content of the liquid slag since in the method of sampling the hot slag was cooled in air. It was noticed, especially in light coloured slags, that the surface of the chilled slag which had come into contact with the air was darker in colour than the remainder of the slag.

The slag analyses have been tabulated both as weight and mole per cent. In the last column of the table the values of K'_{Mn} where $K'_{Mn} = \frac{(\%MnO)}{(\%\ FeO)[\%Mn]}$ have been shown. All the data given refer to an experimental temperature of 1550°C, and the melt numbers missing from the table were melts which were rejected because of crucible failure or because the metal samples were considered unsuitable for analysis because of entrapped slag.

TABLE 3.
Experimental Results at 1550°C.

Run No.	Slag Analysis Weight %						Slag Analysis Mole %				Metal Analysis Weight %				$K'_{Mn} = \frac{(\%MnO)}{(\%FeO)[\%Mn]}$
	SiO_2	ΣFeO	MnO	MgO	Fe_2O_3	FeO	SiO_2	FeO	MnO	MgO	Mn	Oxygen	Si	N	
3	7.5	70.0	12.1	9.7	8.1	62.5	7.85	66.4	10.7	15.2	0.04	0.134	<0.001	N.D.	4.3
4	6.8	55.1	28.1	9.1	5.2	50.5	7.55	50.9	26.4	15.2	0.12	0.097	0.002	N.D.	4.3
5	8.8	27.1	58.0	5.1	2.35	25.2	10.0	25.6	55.7	8.6	0.46	0.050	0.005	N.D.	4.7
6	13.6	26.5	52.5	4.6	2.15	24.4	15.7	25.4	51.0	7.95	0.41	0.0495	0.008	N.D.	5.0
7	12.6	40.9	41.0	4.9	3.55	37.7	14.2	38.5	39.0	8.3	0.21	0.078	0.002	N.D.	5.0
8	16.4	32.9	44.0	6.1	3.05	30.2	18.3	30.2	41.3	10.1	0.23	0.063	0.003	N.D.	6.1
9	13.5	62.8	12.1	11.1	5.9	57.6	14.7	56.4	11.0	17.9	0.032	0.124	N.D.	N.D.	6.1
10	19.4	39.0	30.2	9.7	4.2	35.8	21.1	35.4	27.8	15.8	0.095	0.073	0.007	N.D.	8.1
11	3.8	77.0	14.5	4.0	7.2	70.5	4.38	74.3	14.2	7.0	0.055	0.143	N.D.	N.D.	3.8
13	16.5	46.5	31.1	5.7	4.2	42.7	18.4	42.8	29.3	9.5	0.13	0.107	N.D.	N.D.	5.2
14	24.05	1.9	68.0	6.1	nil	1.9	25.2	1.64	60.4	9.6	4.8	0.0065	N.D.	N.D.	7.5
15	26.9	8.05	54.0	10.1	0.4	7.65	28.6	7.1	48.2	16.1	0.85	0.0238	0.018	0.033	8.4
16	18.8	24.0	47.1	10.2	1.6	22.55	20.0	21.3	42.3	16.4	0.34	0.051	0.004	N.D.	5.8
17	39.0	2.74	35.0	23.1	nil	2.74	37.0	2.16	28.1	32.6	1.15	N.D.	N.D.	N.D.	11.8
18	26.2	20.5	37.0	15.7	1.1	19.5	26.7	17.4	31.8	24.1	0.32	0.040	0.004	N.D.	7.8
19	16.4	62.0	15.1	6.5	5.1	57.4	18.2	57.0	14.0	10.7	0.045	0.120	N.D.	N.D.	5.4
21	16.5	7.5	48.0	26.0	0.4	7.1	16.0	6.65	39.4	38.0	1.11	0.021	0.005	0.040	6.0
26	16.0	41.5	34.5	8.4	3.1	38.7	18.0	38.8	29.2	14.1	0.13	0.085	0.006	0.022	6.4
27	12.9	46.3	32.2	8.6	4.1	42.6	14.1	42.0	29.7	14.1	0.15	0.0965	0.004	0.024	4.7
28	29.24	5.75	43.8	19.7	0.15	5.6	29.0	4.8	36.9	29.4	0.82	0.0103	0.042	0.045	9.3
29	21.4	41.0	24.3	12.8	2.4	38.84	21.8	35.9	20.9	22.6	0.075	0.085	0.003	0.038	7.9
30	21.16	32.4	33.2	12.6	1.85	30.74	22.4	28.1	29.6	20.0	0.14	0.0590	0.007	0.033	7.5
31	27.1	21.1	31.6	19.1	0.9	20.29	27.1	17.6	26.7	28.6	0.17	0.0460	0.003	0.037	8.8
32	22.6	13.05	45.3	18.0	0.8	12.3	22.9	11.0	38.8	27.4	0.39	0.0297	0.002	0.048	8.8
34	27.1	5.75	49.0	16.1	N.D.	5.75	27.8	4.9	42.5	24.8	1.05	0.0185	0.030	0.047	8.1
35	26.1	20.9	29.8	22.1	0.85	20.24	25.6	17.05	24.8	32.6	0.15	N.D.	N.D.	N.D.	9.7
37	27.2	21.0	26.8	18.2	1.1	26.0	27.3	22.6	22.8	27.4	0.13	0.0590	0.002	0.037	7.6
38	0.41	75.6	21.4	1.6	6.5	69.7	0.49	75.0	21.5	2.85	0.075	0.139	<0.001	0.029	3.8
39	9.2	45.5	37.4	7.6	3.9	43.0	10.2	42.0	35.1	12.7	0.20	0.083	0.002	0.030	4.1

TABLE 3 (continued)

Run No.	Slag Analysis Weight %						Slag Analysis Mole %				Metal Analysis Weight %				$K'_{Mn} = \frac{(\%MnO)}{(\%FeO)[\%Mn]}$
	SiO_2	ΣFeO	MnO	MgO	Fe_2O_3	FeO	SiO_2	FeO	MnO	MgO	Mn	Oxygen	Si	N	
40	0.40	68.4	28.2	2.3	6.6	62.45	0.49	67.4	28.1	4.0	0.13	0.120	<0.001	N.D.	3.2
41	15.42	43.8	33.1	6.3	3.8	40.4	17.3	40.8	31.4	10.5	0.125	0.088	0.002	0.027	6.7
42	36.5	2.3	25.3	32.0	nil	2.3	34.0	1.78	19.9	44.3	0.75	0.0028	0.79	N.D.	14.5
43	0.32	81.5	13.6	3.6	7.8	74.5	0.38	79.9	13.55	6.34	0.048	0.157	N.D.	N.D.	3.5
45	13.16	39.5	40.1	6.2	3.53	36.5	14.8	36.8	38.0	10.4	0.18	N.D.	N.D.	N.D.	5.6
48	26.7	18.5	38.4	14.1	1.33	17.3	28.0	16.1	33.9	22.0	0.32	0.042	0.007	N.D.	6.5
47	0.21	94.6	nil	3.6	8.8	86.7	0.25	93.55	nil	6.2	nil	0.191	N.D.	N.D.	—
50	13.9	61.3	18.2	6.3	5.8	56.1	15.5	56.8	17.1	10.6	0.049	0.120	<0.001	0.012	6.1
51	15.9	59.4	14.9	7.9	5.8	54.9	17.7	55.1	14.0	13.2	0.037	0.118	<0.001	0.011	6.8
52	19.8	51.1	16.1	12.5	4.3	47.2	20.9	45.0	14.4	19.7	0.035	0.110	<0.001	0.023	9.0
53	28.0	4.3	49.1	17.85	nil	4.3	28.1	3.61	41.5	26.7	1.20	0.0145	0.020	0.043	9.5
54	26.6	17.1	42.7	13.5	0.65	16.51	27.4	14.7	37.1	20.8	0.30	0.0505	0.005	0.024	8.4
55	34.22	16.2	29.2	19.5	0.66	15.6	33.6	13.26	24.3	28.8	0.185	0.044	0.014	0.040	9.8
57	23.2	26.6	32.1	17.5	2.1	24.7	23.3	22.3	27.3	27.1	0.14	0.067	0.005	0.012	8.6
58	24.65	24.7	34.4	15.7	2.0	22.9	25.2	21.1	29.6	24.1	0.175	0.055	0.005	0.027	8.2
59	22.6	20.5	43.2	13.3	1.6	19.06	23.4	17.8	38.0	20.8	0.26	0.040	0.005	0.036	8.1
60	49.1	13.7	36.5	N.D.	N.D.	N.D.	53.5	12.5	34.0	N.D.	0.18	0.020	0.035	N.D.	14.8
61	25.1	22.8	41.5	10.2	1.3	21.6	26.5	20.1	37.1	16.2	0.21	0.049	0.004	0.035	8.7
62	50.5	19.0	30.6	N.D.	N.D.	N.D.	54.5	17.2	28.2	N.D.	0.11	0.027	0.021	N.D.	14.6
63	49.9	25.6	24.1	N.D.	N.D.	N.D.	54.3	23.4	22.3	N.D.	0.062	0.040	0.010	N.D.	15.4
64	49.7	34.0	15.7	N.D.	N.D.	N.D.	54.1	31.1	14.8	N.D.	0.031	0.050	0.005	N.D.	14.9
65	39.8	8.9	20.2	30.1	N.D.	8.9	36.0	6.85	15.7	42.4	0.17	0.018	0.026	N.D.	13.3
66	49.6	11.5	38.9	N.D.	N.D.	N.D.	54.0	10.4	35.6	N.D.	0.20	0.018	0.034	N.D.	16.8
67	49.7	14.2	36.3	N.D.	N.D.	N.D.	54.0	12.9	33.1	N.D.	0.16	0.022	0.023	N.D.	16.0
68	49.6	16.9	33.5	N.D.	N.D.	N.D.	54.0	15.3	30.7	N.D.	0.12	0.025	0.018	N.D.	16.5

11. Equilibrium in slags relatively free of silica.

Several melts were made in which no silica was included in the slag addition; the data for these melts is shown in Table 4.

Table 4.
Melts made without silica addition (1550°C).

Melt No.	SiO_2	FeO	Mn	O	$K'_{Mn} = \frac{(\%MnO)}{(\%FeO)[\%Mn]}$	$\frac{[O]}{(FeO)}$
	mole fraction		Weight %			
11	0·044	0·743	0·055	0·143	3·8	0·194
38	0·0049	0·750	0·075	0·139	3·8	0·186
40	0·0049	0·674	0·13	0·120	3·2	0·180
43	0·0038	0·799	0·048	0·157	3·5	0·195

Melt No.11 was made using a magnesia crucible made from the less pure magnesia, hence the pick up of 3·8% silica. It appeared that the attack of the slag on these magnesia crucibles was concentrated on the bond, which would be higher in silica than the remainder of the crucible. The other three melts were made in the purer magnesia crucibles and only a small quantity of silica was picked up (<0·5%).

From these melts the average value of K'_{Mn} was 3·6. In melt No.40 in which the value of K_{Mn} was lowest it was noticed that the slag was more viscous than in the other melts. Since this slag had the highest manganous oxide content this was probably due to its composition being near the liquidus composition at 1550°C. Attempts were made to fuse slags with higher manganous oxide contents than this in order to obtain a value for K'_{Mn} with a higher accuracy but a fluid melt could not be obtained.

The average value of K'_{Mn} obtained in this work is compared with those obtained by previous workers in Table 5.

Table 5.
Comparison of values of K'_{Mn}.

Ref.	This work.	Körber and Oelsen(7).	Krings and Schachmann(27).	Gero, Winkler and Chipman(26).
K'_{Mn}	3·6	2·4	3·1	3·8

The value obtained by Gero, Winkler and Chipman(26) was extrapolated from a series of results at higher temperatures using thermodynamic data to calculate the effect of temperature on the equilibrium. The results obtained in this work confirm the value obtained by Gero, Winkler and Chipman rather than that of Körber and Oelsen(7). As already mentioned, the temperature measurements of the latter workers were probably too low.

The ratio $\frac{[\ \%\ \text{oxygen}\ ]}{(\text{mole fraction}\ \Sigma\ FeO)}$ has been calculated and is shown in Table 4 for these melts. This gives an average value of 0·19 for this ratio again agreeing with the data of Gero, Winkler and Chipman and differing from that of Körber and Oelsen(7), who obtained a ratio of 0·24 at 1550°C. Assuming that ferrous oxide behaves ideally in an FeO-MnO slag, the present work indicates that at a mole fraction of FeO of one, molten iron at 1550°C would contain 0·19% oxygen. This value agrees with the oxygen saturation values of Fetters and Chipman(10), Taylor and Chipman(12) and Fischer and von Ende(14) at 1550°C. It also indicates that manganese in the concentrations met with in these melts has no influence on the activity coefficient of oxygen in molten iron.

The variation of oxygen content of molten iron with the manganese content at 1550°C is shown in Fig.12. Above 0·13% manganese the equilibrium is between manganese and oxygen dissolved in liquid iron and solid FeO-MnO slags. If it is assumed that FeO and MnO behave ideally in the solid FeO-MnO slag(this assumption would appear valid because of the similarity of FeO and MnO and that they are probably mutually soluble in the solid state) the oxygen-manganese equilibrium in molten iron with solid FeO-MnO slags can be calculated. In the ensuing discussion the value of 3·6 is taken as the true value of the equilibrium constant $\frac{(a_{MnO})}{a_{FeO}[a_{Mn}]}$ at 1550°C, the standard state of manganese being a 1% solution of manganese in iron.

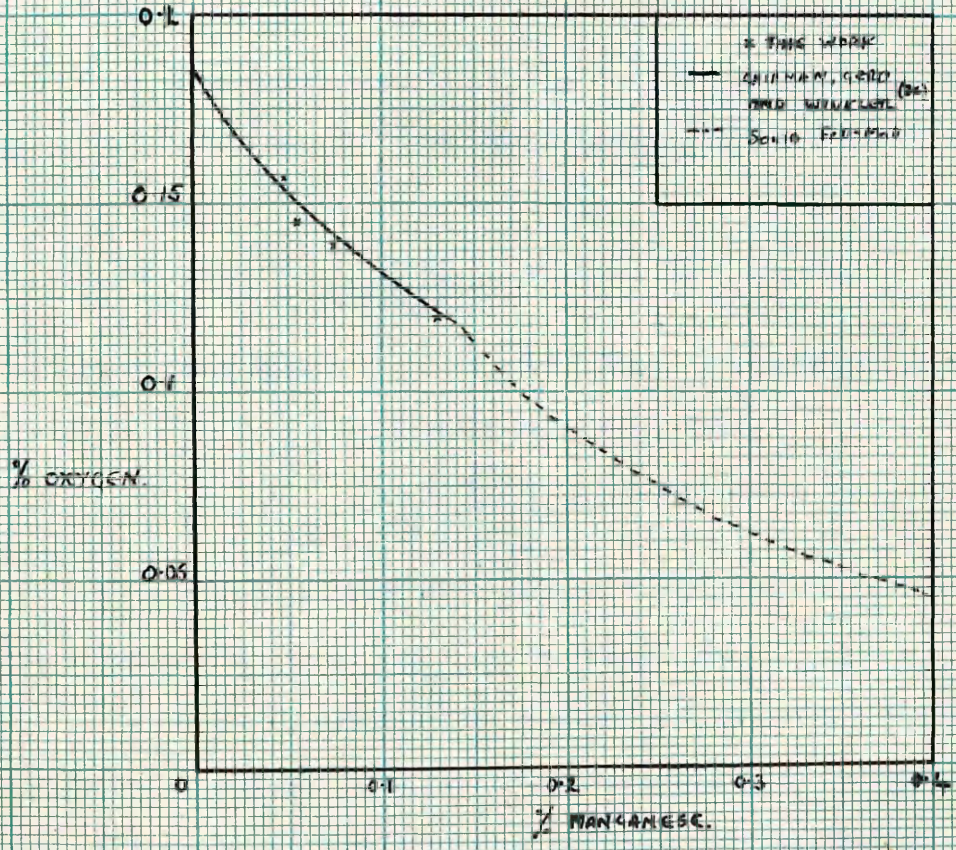


FIG. 12 MANGANESE - OXYGEN EQUILIBRIUM (1550°C)

111. Equilibrium in Melts made in Silica Crucibles.

Several melts were made in silica crucibles to determine the equilibrium between manganese, silicon and oxygen in molten iron with silica saturated FeO-MnO-SiO_2 slags. The data obtained from these melts are shown in Table 6.

From these experiments the average value of K'_{Mn} was 15·6 which agrees well with that of Körber and Oelsen(38) of 15·5 for silica saturated slags.

$$\text{Since} \quad K_{Mn} = \frac{(a_{MnO})}{(a_{FeO})[a_{Mn}]} = 3{\cdot}6$$

If it is assumed that within the above range of concentration manganese behaves ideally in a molten Fe-Si-Mn-O alloy, then

$$\frac{\gamma_{MnO}(MnO)}{\gamma_{FeO}(FeO)[\%Mn]} = 3{\cdot}6$$

From this relation, knowing the activity coefficient of ferrous oxide (γ_{FeO}) that of manganous oxide (γ_{MnO}) can be calculated.

If it is assumed that silicon does not affect the activity coefficient of oxygen in molten iron, the activity of ferrous oxide in the molten slags can be calculated from the partition coefficient

$$\frac{[\%O]}{(a_{FeO})} = 0{\cdot}19 \quad \text{at} \quad 1550^{\circ}C.$$

Values calculated from this relation are given in Table 6, and indicate an average value for γ_{FeO} of 0·87.

Table 6.

Melts made in Silica Crucibles.

Melt No.	ΣFeO mole fraction	Mn	Si	O	K'_{Mn}	$K_{Si} = [O]^2[Si] \times 10^5$	$a_{FeO} = \frac{[\%O]}{0.19}$	γ_{FeO}	γ_{MnO}	$K_{MnSi} = \frac{[Mn]^2}{(MnO)^2[Si]}$	* $\frac{\gamma_{FeO} f'_o [\%O]}{[.19](\Sigma FeO)}$
		Weight per cent.									
60	0.125	0.18	0.035	0.020	14.8	1.4	0.105	0.84	0.20	8.0	0.74
62	0.172	0.11	0.021	0.027	14.6	1.52	0.141	0.82	0.20	7.3	0.73
63	0.234	0.062	0.010	0.040	15.4	1.60	0.21	0.90	0.21	7.8	0.85
64	0.311	0.031	0.005	0.050	14.9	1.25	0.26	0.85	0.21	8.8	0.85
66	0.104	0.20	0.034	0.018	16.8	1.10	0.095	0.91	0.19	9.3	0.77
67	0.129	0.16	0.023	0.022	16.0	1.10	0.116	0.90	0.20	9.1	0.81
68	0.153	0.12	0.018	0.025	16.5	1.13	0.132	0.86	0.19	8.5	0.82

Chipman and Gokcen(35) found that silicon affected the activity of oxygen in molten iron and gave the effect of silicon on the activity coefficient of oxygen (f_O^{Si}) as 0·82 for 0·04% silicon at 1545°C. This data has been withdrawn in a revision(35a) of the paper as Chipman and Gokcen(35a) believed it did not fit with the work of Dastur and Chipman(9). If this effect is applied to the calculation of γ_{FeO} the partition coefficient is

$$\frac{f_O^{Si}[\%O]}{(a_{FeO})} = 0{\cdot}19 \text{ at } 1550^{\circ}C$$

Values of γ_{FeO} using Chipman and Gokcen's data are also shown in Table 6 and indicate γ_{FeO} equal to 0·80 at 1550°C.

Over the range of compositions studied and considering the small number of melts made, no reliable conclusions could be drawn as to any variation in γ_{FeO} with the MnO content of the slags. A study of the data of Körber and Oelsen(38) for this equilibrium also does not indicate any variation in γ_{FeO} with slag composition, although when the amount of scatter they obtained is considered a small variation might escape notice.

In comparing Körber and Oelsen's data on a_{FeO} in silica-saturated FeO-MnO-SiO_2 slags with the present work the difficulty of choosing an oxygen saturation figure arises. Körber and Oelsen(7) in their earlier work on FeO-MnO slags reported this as 0·24% at 1550°C and the disagreement with results obtained in other work(10)(15) has been attributed to errors in temperature measurement. Using this figure for oxygen saturation the activity coefficient of ferrous oxide in Körber and Oelsens' silica saturated slags would be 0·71.. However, as the value of K'_{Mn} obtained in the present work agrees with that obtained by Körber and Oelsen it would appear that

the temperature measurements in their work on silica saturated slags were correct. Their value of 0·24% for the solubility of oxygen in iron at 1550°C is almost certainly too high and when 0·19% is used, 0·9 is obtained for γ_{FeO} in these slags (neglecting any effect of silicon on the activity coefficient of oxygen). This figure agrees with that of 0·87 obtained in the present work.

Applying the data on f_o^{C} obtained by Gokcen and Chipman reduces γ_{FeO} calculated from Körber and Oelsen from 0·9 to approximately 0·82, but the scatter of results is too great to detect any effect of silicon on f_o.

Gokcen and Chipman have given a_{FeO} in silica-saturated $FeO-SiO_2$ slags as 0·39 at 1600°C, Schuhmann and Ensio(33) as 0·377 at the melting point of iron and Fischer and vom Ende(14) 0·43 at 1550°C, corresponding to γ_{FeO} equal to 0·83, 0·81 and 0·90 respectively. These results when compared with those of the present work indicate that manganous oxide has no great effect on γ_{FeO} in silica-saturated $FeO-MnO-SiO_2$ slags.

γ_{MnO} for the silica saturated melts has been calculated and is shown in Table 6, giving an average value of 0·20. Körber and Oelsen's data indicate a value of 0·21 (taking $\gamma_{FeO} = 0·9$) which is in good agreement with the present work. Thus silica has a much greater effect on γ_{MnO} than on γ_{FeO}, a result which is consistent with the cation-oxygen bond strengths of Fe^{++} and Mn^{++}.

A value for the equilibrium constant for the reaction between silicon and oxygen in molten iron

$$Si_{(Fe)} + 2\,O_{(Fe)} \rightleftharpoons SiO_{2\,(CRIST.)} \qquad K_{Si} = [\%Si][\%O]^2$$

has also been obtained from the above data. As a silica crucible was used

the activity of silica has been taken as unity. The values calculated for this equilibrium constant are given in Table 6 and the average value obtained is compared with previous work in Table 7.

Table 7.
Comparison of values of K_{Si} obtained by different workers.

Reference	Present Work.	Körber and Oelsen(38)	Hilty and Crafts(29)	Chipman and Gokcen(35a)
$K_{Si} = [\%Si][\%O]^2$	1.3×10^{-5}	1.34×10^{-5}	1.6×10^{-5}	1.1×10^{-5}

The value of Chipman and Gokcen(35a) is a revised value using new data on the formation of cristobalite. The values obtained here agrees, within the limits of experimental error, with that obtained in other work, and suggests that manganese has little effect on the silicon-oxygen equilibrium at the concentrations encountered in the present work. Körber and Oelsen(38) have used the ratio K'_{MnSi} to express the equilibrium between manganese and silicon dissolved in liquid iron and silica-saturated $FeO-MnO-SiO_2$ slags. Values of this ratio have been calculated and are shown in Table 6. They give an average value for K'_{MnSi} of 8.5×10^{-4} compared with 9.6×10^{-4} obtained by Körber and Oelsen.

Hilty and Crafts(29) plotted the relation between manganese and silicon in liquid iron melted under silica-saturated $FeO-MnO-SiO_2$ slags, taking as their silica-saturated slags the points of inflexion in the

silicon-oxygen plots. Their data is compared with that of Körber and Oelsen and with the results of the present work in Fig.13. This shows that the present work confirms that of Körber and Oelsen but disagrees with that of Hilty and Crafts, the deviations being greatest at low silicon contents. It has already been pointed out (page 19) that the points of inflexion in Hilty and Crafts work are thermodynamically unsound and also that they did not agree with the oxygen values expected for equilibrium with silica saturated slags. This is the probable reason for the disagreement between the present work and that of Körber and Oelsen with the results of Hilty and Crafts on the manganese-silicon equilibrium. The present work has in the main confirmed that of Körber and Oelsen(38) on silica saturated FeO-MnO-SiO_2 slags at 1550°C. It is therefore of interest to consider the effect of temperature on the activities of FeO and MnO in silica saturated slags, which may be calculated from the results of Körber and Oelsen(38), Chipman, Gero and Winkler(36) and Taylor and Chipman(13), obtained at temperatures other than 1550°C.

Table 8.

Temperature °C.	(26) K_{Mn}	(13) $\frac{[\%O]}{(a_{FeO})}$	(38) K'_{Mn}	(38) $\frac{[\%O]100}{(FeO)}$ Silica-sat.	γ_{FeO} silica-saturated	γ_{MnO} silica-saturated
1600	2·8	0·225	12·0	0·21	0·94	0·22
1650	2·5	0·28	9·0	0·26	0·94	0·26

These calculations indicate that γ_{FeO} does not vary much with temperature but that γ_{MnO} increases with increasing temperature in silica saturated FeO-MnO-SiO_2 slags. In the calculation of γ_{FeO} the effect of silicon on the activity of oxygen in molten iron has been neglected, since the scatter of the values of $\frac{[\%O]}{(FeO)}$ in Körber and Oelsen's work was too large for any effect to be noticed.

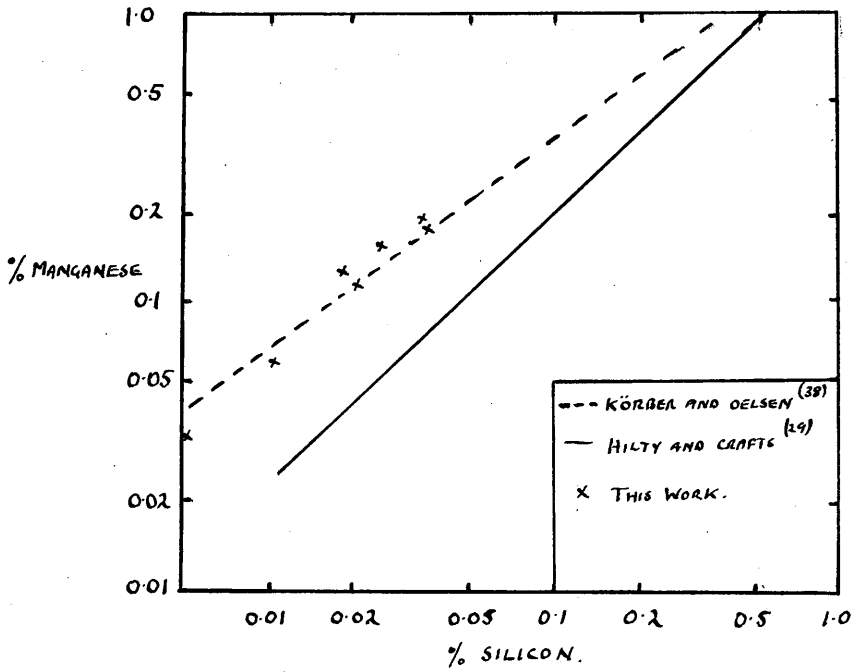


FIG 13 MANGANESE – SILICON EQUILIBRIUM IN MOLTEN IRON AT 1550°C. UNDER SILICA SATURATED $FeO - MnO - SiO_2$ SLAGS.

IV. Equilibrium in melts made in Magnesia Crucibles with Slags containing Silica.

(a) Oxygen equilibrium.

A large number of melts were made to find the effect of silica content on the activity of ferrous oxide in the system $FeO-MnO-SiO_2$. Since magnesia crucibles were used in these melts the slags contained FeO, MgO, MnO and SiO_2. The magnesia pick up of the slags increased with increasing silica content and above 30% silica became too large for slags in the range 30-50% silica to be studied satisfactorily.

The oxygen contents of all the melts made were determined and are plotted in Fig.14 on a ternary diagram as a function of the slag composition with which they were in equilibrium. This has been plotted as a pseudo-ternary system $FeO-(MnO+MgO)-SiO_2$ combining the two basic constituents magnesia and manganous oxide. This form of plot was used as it was impossible to separate the individual effects of MnO and MgO. To construct the diagram the data of Schuhmann and Ensio(33) for the binary system $FeO-SiO_2$ has been used and also the data on silica saturated $FeO-MnO-SiO_2$ slags obtained in the present work. The liquidus at the (MgO+MnO) corner of the system was taken from the diagram $FeO-MnO-SiO_2$ of Carter, Murad and Hay(22). Using all these data, lines of equal oxygen content have been drawn on the diagram which gives the oxygen content of molten iron in equilibrium at 1550°C with $(MnO+MgO)-FeO-SiO_2$ slags.

The activity of ferrous oxide in these slags has been calculated from the oxygen content of the metal assuming that manganese and silicon in the concentrations met with in this work have no effect on the activity coefficient of oxygen in liquid iron. Iso-activity lines for ferrous oxide

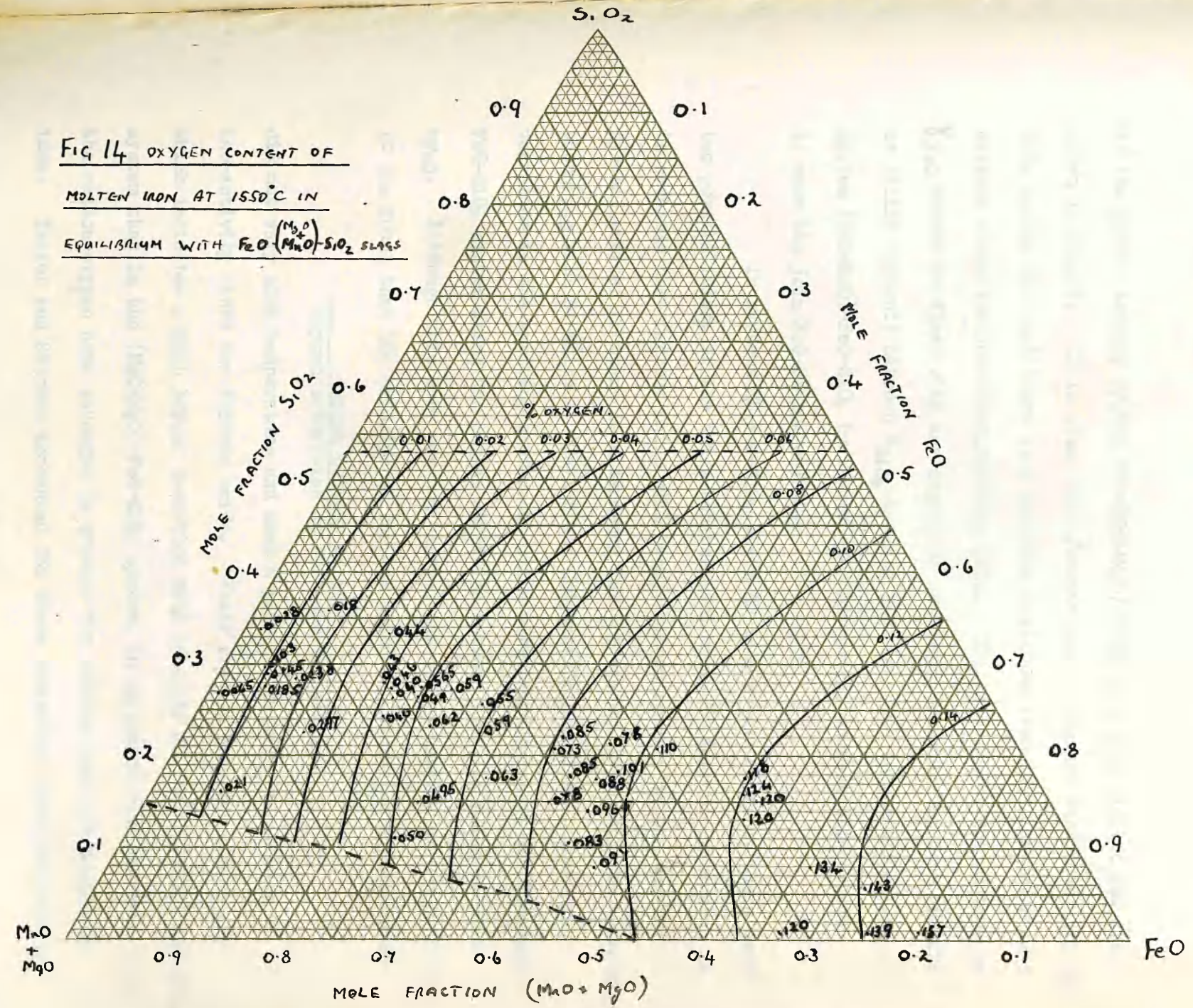


FIG 14 OXYGEN CONTENT OF MOLTEN IRON AT 1550°C IN EQUILIBRIUM WITH $FeO-\frac{(MgO)}{(MnO)}-SiO_2$ SLAGS

in the pseudo ternary system $FeO-(MnO+MgO)-SiO_2$ have been plotted and are shown in Fig.15. It is clear that ferrous oxide does not behave ideally in this system but that there is a positive deviation from ideality which is a maximum along the $FeO-2(MnO,MgO)SiO_2$ join. The location of the maximum in γ_{FeO} cannot be fixed with any degree of certainty owing to the lack of data at silica contents between $N_{SiO_2}=0.4$ and 0.53 but data on the analogous system $(CaO+MgO)-FeO-SiO_2$ by Taylor and Chipman(13) suggest this maximum is near the join $FeO-2(MgO.MnO)SiO_2$.

In systems $MO-FeO-SiO_2$ where MO is a metallic oxide, there exist two possibilities; if the oxide behaves similarily to ferrous oxide then it is probable that ferrous oxide will behave almost ideally in the ternary system, whereas if there is a tendency for the oxides MO and SiO_2 to associate then γ_{FeO} will be raised. Taylor and Chipman(13) have investigated the variation in the activity of ferrous oxide with composition in the $(CaO+MgO)-FeO-SiO_2$ system using the oxygen partition between slag and metal to find a_{FeO}. Although this work was not carried out at any particular temperature it was found that the activity of ferrous oxide as determined by the ratio

$$\frac{\text{oxygen content of iron}}{\text{oxygen saturation at the same temperature}}$$

did not vary with temperature and that a plot could therefore be made of iso-activity lines for ferrous oxide. Their results are shown in Fig.16 which indicates a much larger deviation from ideality in the $(CaO+MgO)-FeO-SiO_2$ system than in the $(MnO+MgO)-FeO-SiO_2$ system, in agreement with the fact that the cation-oxygen bond strength is greater for calcium than for manganese ions. Taylor and Chipman accounted for these deviations from ideality in

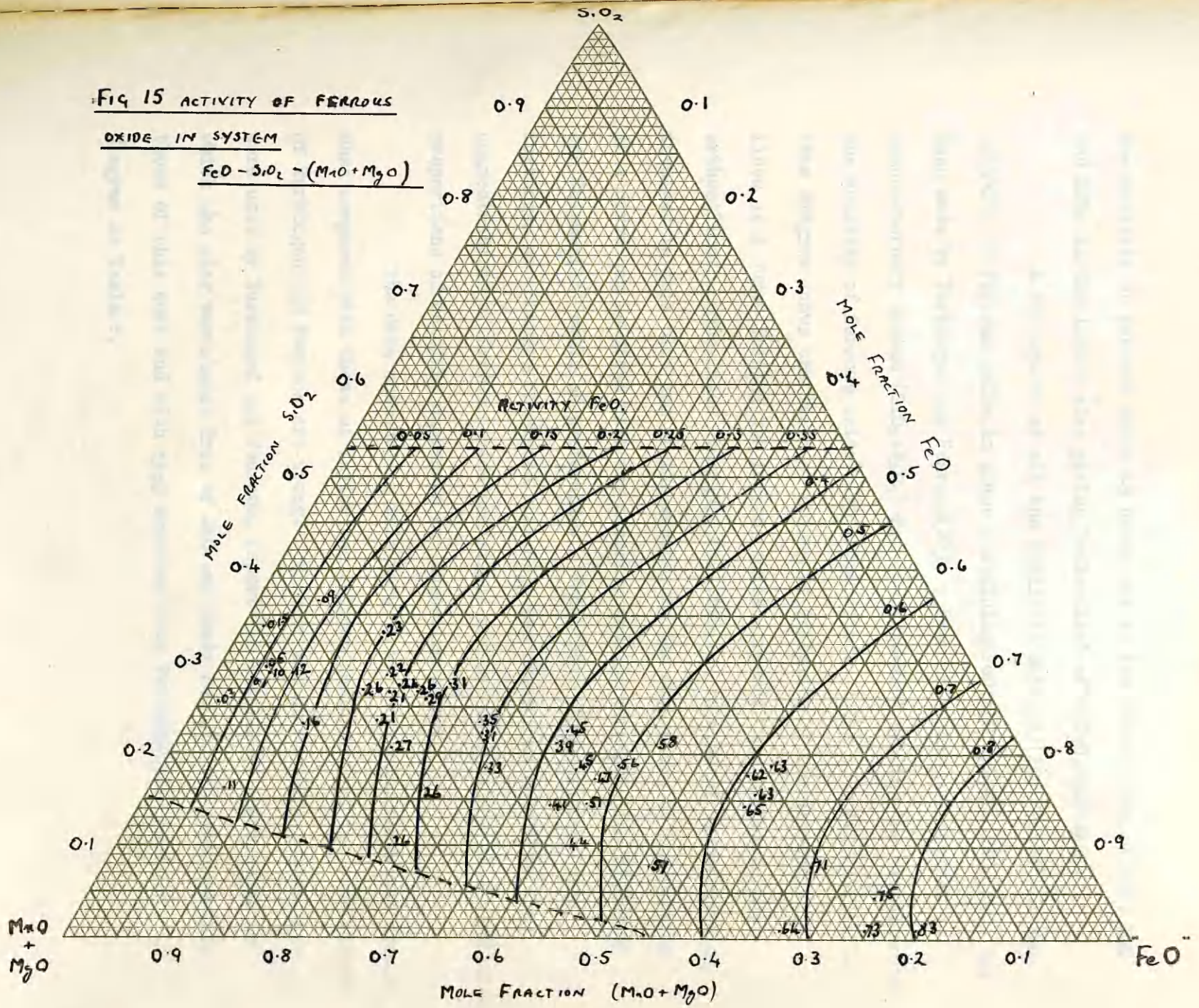


FIG 15 ACTIVITY OF FERROUS OXIDE IN SYSTEM
FeO – SiO2 – (MnO + MgO)
SiO2
MnO + MgO
FeO
MOLE FRACTION SiO2
MOLE FRACTION FeO
MOLE FRACTION (MnO + MgO)
ACTIVITY FeO.
0·05
0·1
0·15
0·2
0·25
0·3
0·35

the activity of ferrous oxide as being due to the association of CaO, MgO and SiO_2 in the liquid slag giving "molecules" of $4(CaO,MgO)2SiO_2$.

A collection of all the available data(13)(28)(33)(35) on the activity of ferrous oxide in slags containing FeO,MgO,CaO,MnO,SiO_2,P_2O_5 has been made by Turkdogan and Pearson(37). From this they constructed a pseudo-ternary system $(SiO_2+P_2O_5)$-FeO-(CaO+MgO+MnO) showing the variation in the activity of ferrous oxide with composition. This is shown in Fig.17. This diagram shows the locus of points of inflexion of the iso-activity lines as a curve joining the ferrous oxide corner of the system to the orthosilicate composition $2(CaO,MgO,MnO).SiO_2$. In view of the assumption involved in this plot and of the scatter in the data used, it is doubtful if a curve can be drawn with any accuracy and the straight line of Taylor and Chipman(13) would be preferable. From their study of these data Turkdogan and Pearson concluded that a_{FeO} was determined solely by the concentrations of ferrous oxide and silica and was independent of the relative proportions of calcium, manganese and magnesium oxides.

The data obtained in this work in which calcium oxide was absent when compared with those of Taylor and Chipman indicate that the conclusions of Turkdogan and Pearson are wrong. Winkler and Chipman(28), whose data were used by Turkdogan and Pearson, report the results of three melts in which the slag was almost free of CaO and their results are compared with those of this work and with a_{FeO} expected from Turkdogan and Pearson's diagram in Table 8.

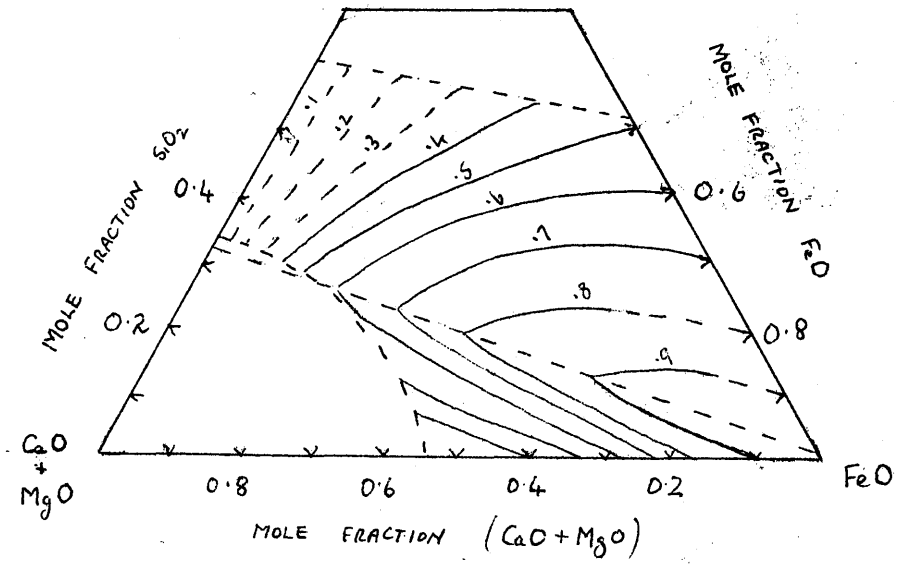


Fig 16 ACTIVITY OF FeO IN $(CaO + MgO) - FeO - SiO_2$ SYSTEM [13]

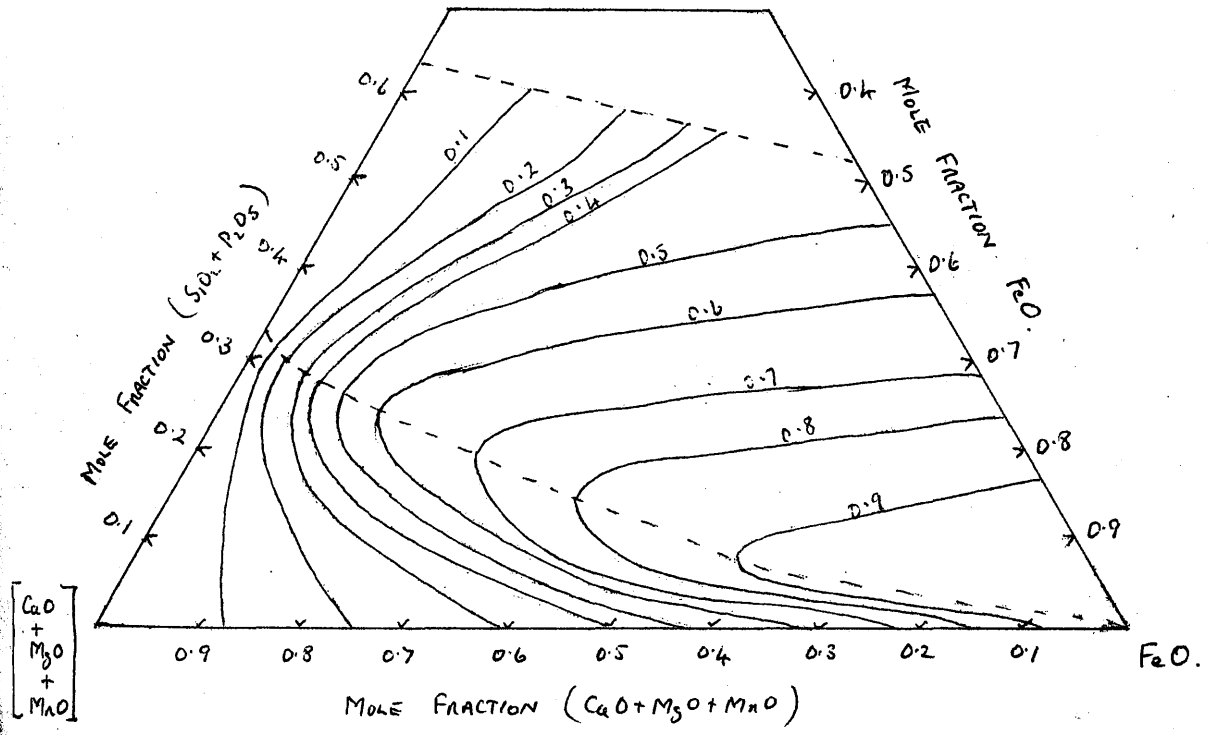


Fig 17 ACTIVITY OF FeO IN $(CaO + MgO + MnO) - FeO - (SiO_2 + P_2O_5)$ SYSTEM [37]

Table 8.
Comparison of a_{FeO} in FeO-(MnO+MgO)-SiO_2 System.

Slag composition Mole % Winkler and Chipman(28)			Activity of Ferrous Oxide		
Σ FeO	MnO+MgO	SiO_2	Winkler and Chipman(28)	This Work	Turkdogan and Pearson (37).
39.8	45	14.8	0.45	0.45	0.82
24.8	52.2	23.0	0.38	0.32	0.69
22.8	54.1	22.95	0.32	0.30	0.68

This shows that Winkler and Chipman's results agree with those obtained in this work and are very much lower than would be expected from Turkdogan and Pearson's assumption. Their assumption is probably a reasonable approximation as far as steelmaking slags are concerned, where the concentrations of CaO, MgO and MnO only vary within a limited range, but once it is removed from these limits it is erroneous and cannot explain the a_{FeO} in the (MnO+MgO)-FeO-SiO_2 system.

As the effect of magnesia on a_{FeO} cannot be separated from that of manganous oxide in this work the data on the system (MnO-MgO)-FeO-SiO_2 has been used to give an approximation to the a_{FeO} in the MnO-FeO-SiO_2 system by assuming that MgO and MnO have a similar effect.

Schenck(42) using his dissociation constants for slag components has calculated the variation of the activity of ferrous oxide with composition in the FeO-MnO-SiO_2 system. This diagram, shown in Fig.9 indicates a reduction in the activity coefficient of ferrous oxide with increasing silica in the system, as against the increase found in this work. This indicates

TABLE 9.

Ratio of Ferric to Ferrous Oxide in Melts.

Melt No.	SiO_2 %	FeO %	$\frac{Fe_2O_3}{FeO}$	Melt No.	SiO_2 %	FeO %	$\frac{Fe_2O_3}{FeO}$
3	7·5	70·0	0·13	32	22.6	13.05	0.065
4	6.8	55.1	0.10	34	27.1	5.75	-
5	8.8	27.1	0.093	35	26.1	20.9	0.045
6	13.6	26.5	0.089	37	27.2	27.0	0.043
7	12.6	40.9	0.094	38	0.41	75.6	0.093
8	16.4	32.9	0.10	39	9.20	45.5	0.090
9	13.5	62.8	0.10	40	0.40	68.4	0.10
10	19.4	39.0	0.11	41	15.42	43.8	0.094
11	3.8	77.0	0.10	42	36.5	2.3	-
13	16.5	46.5	0.099	43	0.32	81.5	0.10
14	24.05	1.9	-	45	13.16	39.5	0.097
15	26.9	8.05	0.052	48	26.7	18.5	0.077
16	18.8	24.0	0.071	47	0.21	94.6	0.10
17	39.0	2.74	-	50	13.9	61.3	0.10
18	26.2	20.5	0.057	51	15.9	59.4	0.10
19	16.4	62.0	0.089	52	19.8	51.1	0.09
21	16.5	7.5	0.056	53	28.0	4.3	-
26	16.0	41.5	0.080	54	26.6	17.1	0.040
27	12.9	46.3	0.096	55	34.22	16.2	0.042
28	29.24	5.75	0.027	57	23.2	26.6	0.085
29	21.4	41.0	0.062	58	24.65	24.7	0.087
30	21.16	32.4	0.060	59	22.6	20.5	0.083
31	27.1	21.1	0.045	61	25.1	22.8	0.063

that the assumption of compounds as applied by Schenck is not applicable to the $FeO-MnO-SiO_2$ system.

Flood, Forland and Grjotheim(47) have put forward the equation

$$RT \ln \gamma_{FeO} = 15 N'_{Ca^{++}} N'_{SiO_4^{4-}} + 9 N'_{Mg^{++}} N'_{SiO_4^{4-}}$$

based on Flood's conception of ionic fraction to express the effect of calcium oxide and magnesia on the activity coefficient of ferrous oxide in the system $(CaO+MgO)-FeO-SiO_2$ at 1600°C. On the same basis the activity coefficient in the $(MnO+MgO)-FeO-SiO_2$ system would be

$$RT \ln \gamma_{FeO} = x N'_{Mn^{++}} N'_{SiO_4^{4-}} + 9 N'_{Mg^{++}} N'_{SiO_4^{4-}}$$

where x Kcal. is the free energy change for the reaction

$$FeO = \tfrac{1}{2} Mn_2 SiO_4 \rightleftharpoons \tfrac{1}{2} Fe_2SiO_4 + MnO$$

Since the free energy of formation of $2MnO.SiO_2$ is not known this equation cannot be compared with the data, although it indicates that it would be less than that of $2CaO.SiO_2$.

In the diagram(Fig.13) and the discussion of the activity of ferrous oxide the ferrous oxide content of the slag has been calculated from the iron content of the slag. This method was used as all comparative data were based on this same assumption; but analysis of the slags has shown that varying amount of ferric oxide were present in the melts. These are shown in Table 3 and as Fe_2O_3/FeO ratio in Table 9. Darken and Gurry(1) have given the ratio Fe_2O_3/FeO as 0·0525 in ferrous oxide melted in iron crucibles, but Chipman and Fetters(10) found that melting in magnesia crucibles raised the proportion of ferric oxide, a finding which is confirmed here. Darken and Gurry(25) have also shown that manganous oxide has a tendency to stabilise ferric oxide and the combined effect of MnO and MgO

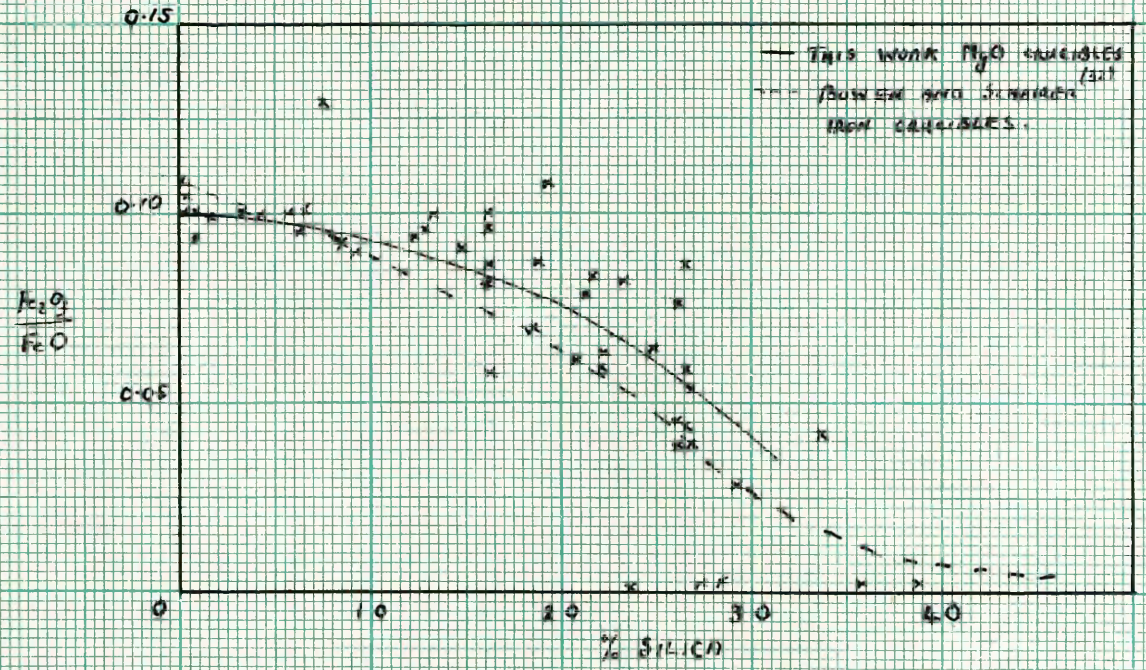


FIG 18 EFFECT OF SiO_2 ON Fe_2O_3 CONTENT OF SLAGS.

probably accounts for the higher ratio Fe_2O_3/FeO found in this work. The effect of calcium oxide is greater than that of either magnesia or manganous oxide and this is illustrated in Winkler and Chipmans(28) work where much higher ratios were found.

The ratio of ferric to ferrous oxide was found to decrease with silica content and this is illustrated in Fig.18 where the ratio is plotted against the silica content of the slags. Silica as would be expected has the opposite effect to the basic oxides; this was also found by Bowen and Schairer(32) in their study of the $FeO-SiO_2$ diagram, and by White(43) in his study of the dissociation of iron oxide in the presence of silica and of lime.

In the course of the oxygen analyses of the melts some data on the nitrogen contents were obtained; these are plotted in Fig.19 which shows that the oxygen and nitrogen contents of the melts were related. Since the melts were made in a nitrogen atmosphere it would be expected that they would be saturated with nitrogen (0·042% at 1550°C) but Fig.19 indicates that the nitrogen pick up decreased as the oxygen content of the melts increased and saturation was only approached at low oxygen contents (0·04%). It appears that oxygen either reduces the solubility of nitrogen in iron or that it reduces the rate at which nitrogen dissolves in iron by affecting its rate of diffusion. This confirms the data obtained in Bessemer made steel where at the end of the blow it would be expected that nitrogen saturation would be reached but this is not the case and the observed nitrogen content is lower than would be expected. It has been suggested that this is due to liquid oxide films but both carbon and silicon have been found to lower the solubility of nitrogen in liquid iron(67); it may be that oxygen has a similar effect. The effect of carbon is compared with that of oxygen in Fig.19.

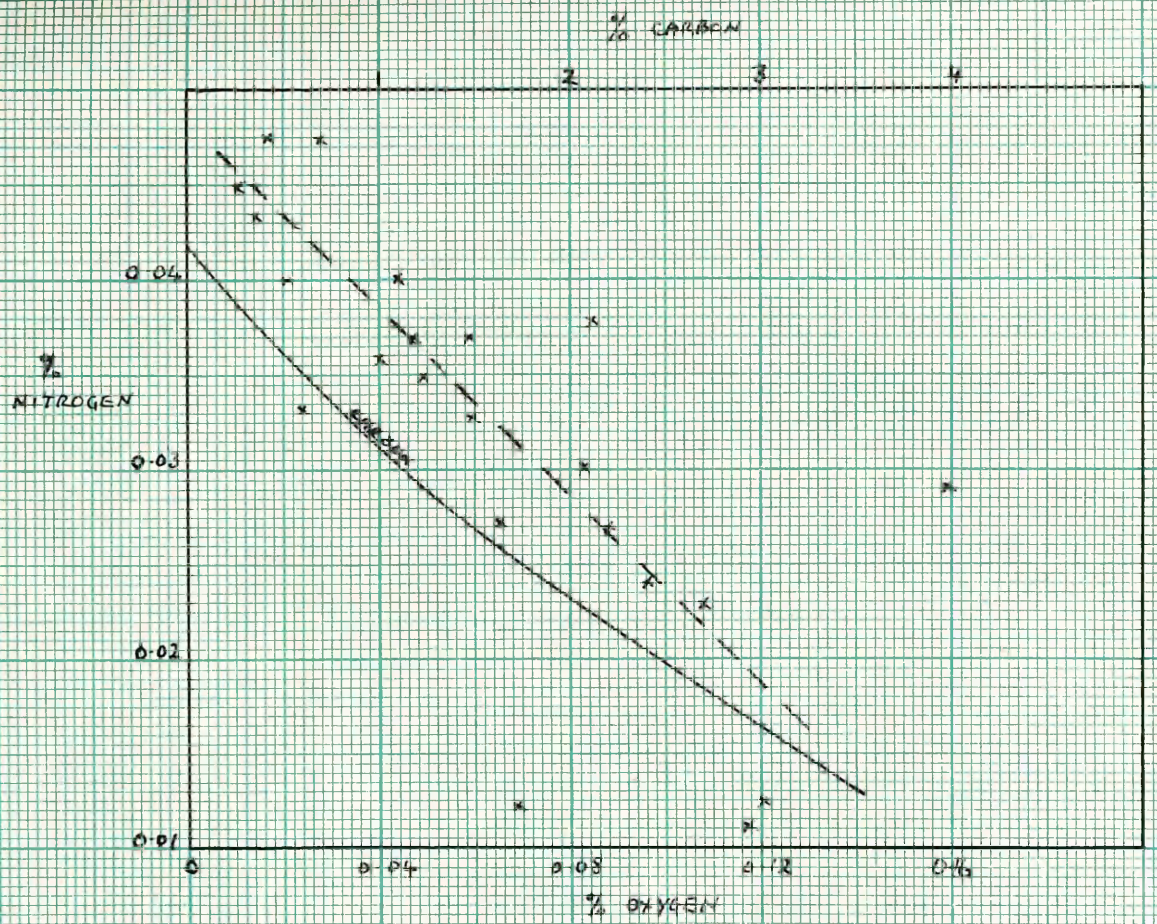


FIG 19 VARIATION OF NITROGEN CONTENT OF MELTS WITH THE OXYGEN CONTENT

(b) Manganese Equilibrium.

From the melts made in magnesia crucibles the effect of silica content on the equilibrium

$$Mn + FeO \rightleftharpoons MnO + Fe$$

between molten iron containing manganese, silicon and oxygen and $FeO-MnO-SiO_2$ slags has been studied.

The results for K'_{Mn} have been tabulated in Table 3 and are plotted in Fig.20 as a function of the silica content of the slag expressed as weight per cent. The values of K'_{Mn} at 0% and 50% silica have been taken from the results already discussed for pure oxide and silica saturated slags. In Fig.21 K'_{Mn} has been plotted against the mole fraction of silica in the slags. Both curves show that K'_{Mn} increases as the silica content of the slag increases up to saturation.

Results of experiments carried out by Krings and Schackmann(27) in alumina crucibles - alumina was therefore present in their slags - are also plotted in Figs.20 and 21. The agreement with the present work is good especially since different crucible materials were used. The largest deviations are at the higher silica contents where Krings and Schackmann obtained lower K'_{Mn} values for equivalent silica contents than were obtained in the present work. In the $FeO-Al_2O_3-SiO_2$ system silica saturation occurs at a higher concentration of silica than in the $FeO-MgO-SiO_2$ system and a similar difference probably exists between the $FeO-MnO-Al_2O_3-SiO_2$ and $FeO-MnO-MgO-SiO_2$ systems. This probably accounts for the differences between these two sets of results, in that K'_{Mn} would increase more slowly with increasing silica in slags containing alumina than in slags containing magnesia.

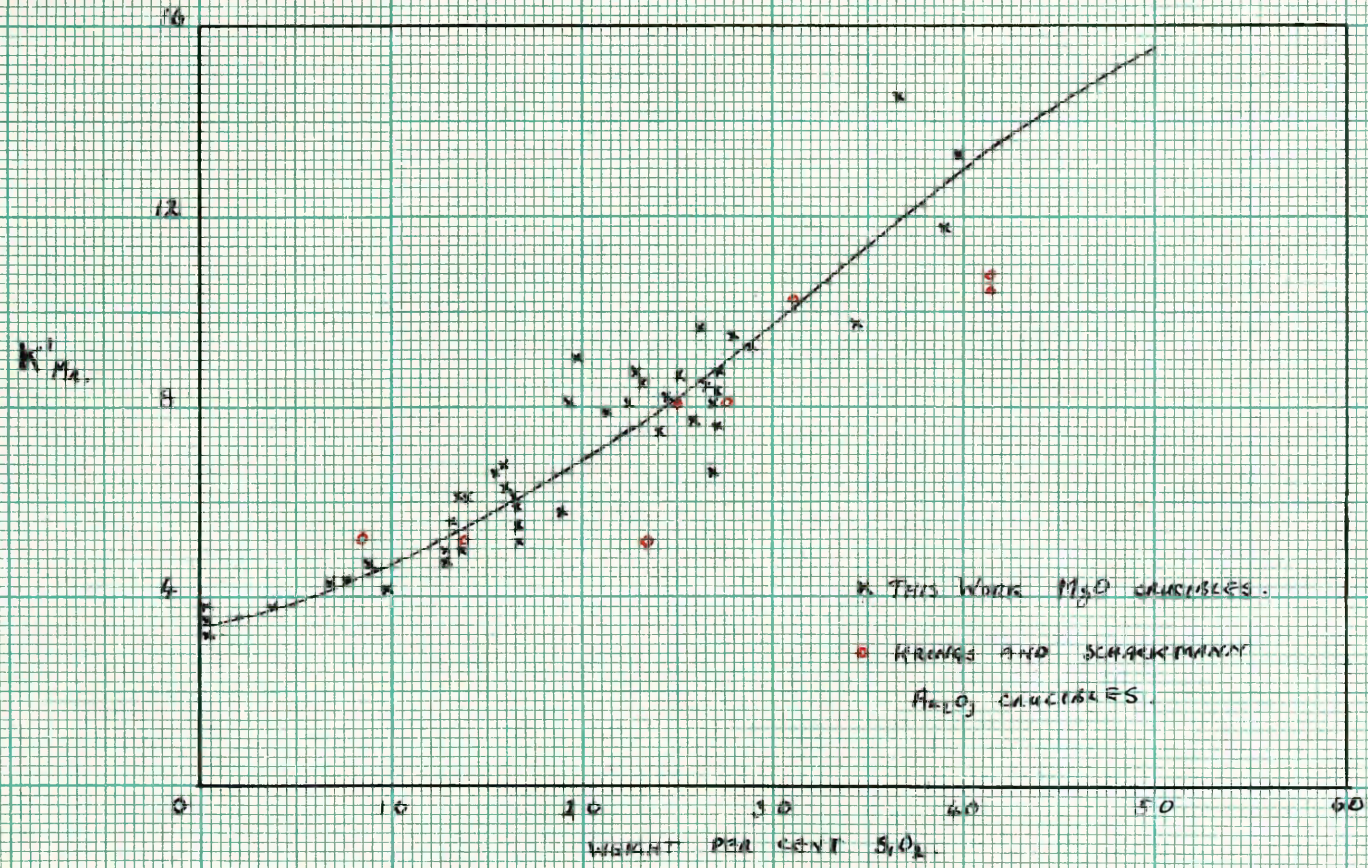


FIG 2D VARIATION OF K'_{Mn} WITH WEIGHT PER CENT SILICA (1550°C)

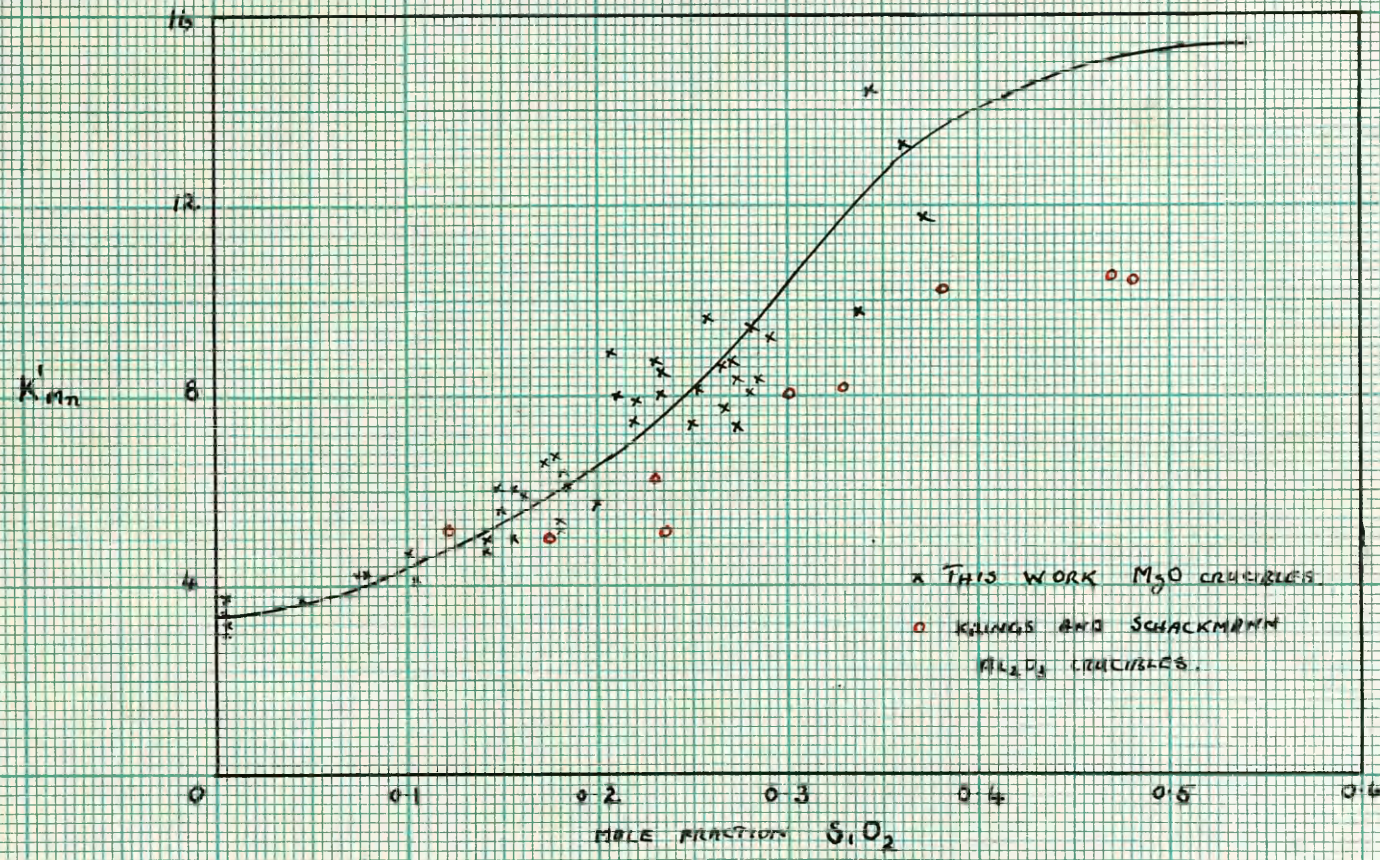


FIG. 21 VARIATION OF K'_{Mn} WITH MOLE FRACTION SILICA (1550 °C)

The slag data of Hilty and Crafts(29) show too large a scatter in K'_{Mn} for any conclusions or comparisons to be made as to the influence of silica on the value of K'_{Mn}.

As in the previous discussion the equilibrium

$$K_{Mn} = \frac{\gamma_{MnO}\,(MnO)}{(a_{FeO})[\%Mn]} = 3{\cdot}6 \text{ at } 1550^{\circ}C$$

must obtain. Using the data on the activity of ferrous oxide in these slags summarised in Fig.15, the activity coefficient of manganous oxide can be calculated from $\gamma_{MnO} = \frac{3{\cdot}6\ a_{FeO}}{K'_{Mn}\,(FeO)}$. To calculate γ_{MnO} a plot has been made of the ratio $\frac{(\text{mole fraction } MnO)}{(a_{FeO})\,[\%Mn]}$ against the silica concentration expressed as a mole fraction and shown in Fig.22. Using this plot γ_{MnO} can be calculated at any given silica content. Since K'_{Mn} at any given silica content was independent of the ratio FeO/MnO of the slag within the limits of experimental error, the activity coefficient of manganous oxide was assumed to be dependent solely on the silica content of the slag.

In this discussion of the activity of manganous oxide in these slags magnesia has been treated as a diluent. This can only be a first approximation especially in the slags with more than 20% silica where the magnesia contents were fairly high; however, physical measurements on liquid silicates such as viscosity(60), surface tension(61) and electrical conductivity(62) suggest that the effect of basic ions on the liquid silicate structure decreases in the order Ca++, Mn++, Fe++, Mg++.

The values of γ_{MnO} calculated from K'_{Mn} and a_{FeO} have been used to give approximate values for the activity of manganous oxide in the binary system $MnO\text{-}SiO_2$ shown in Fig.23. At high manganous oxide contents these slags are partially solid at 1550°C and the activities therefore refer to

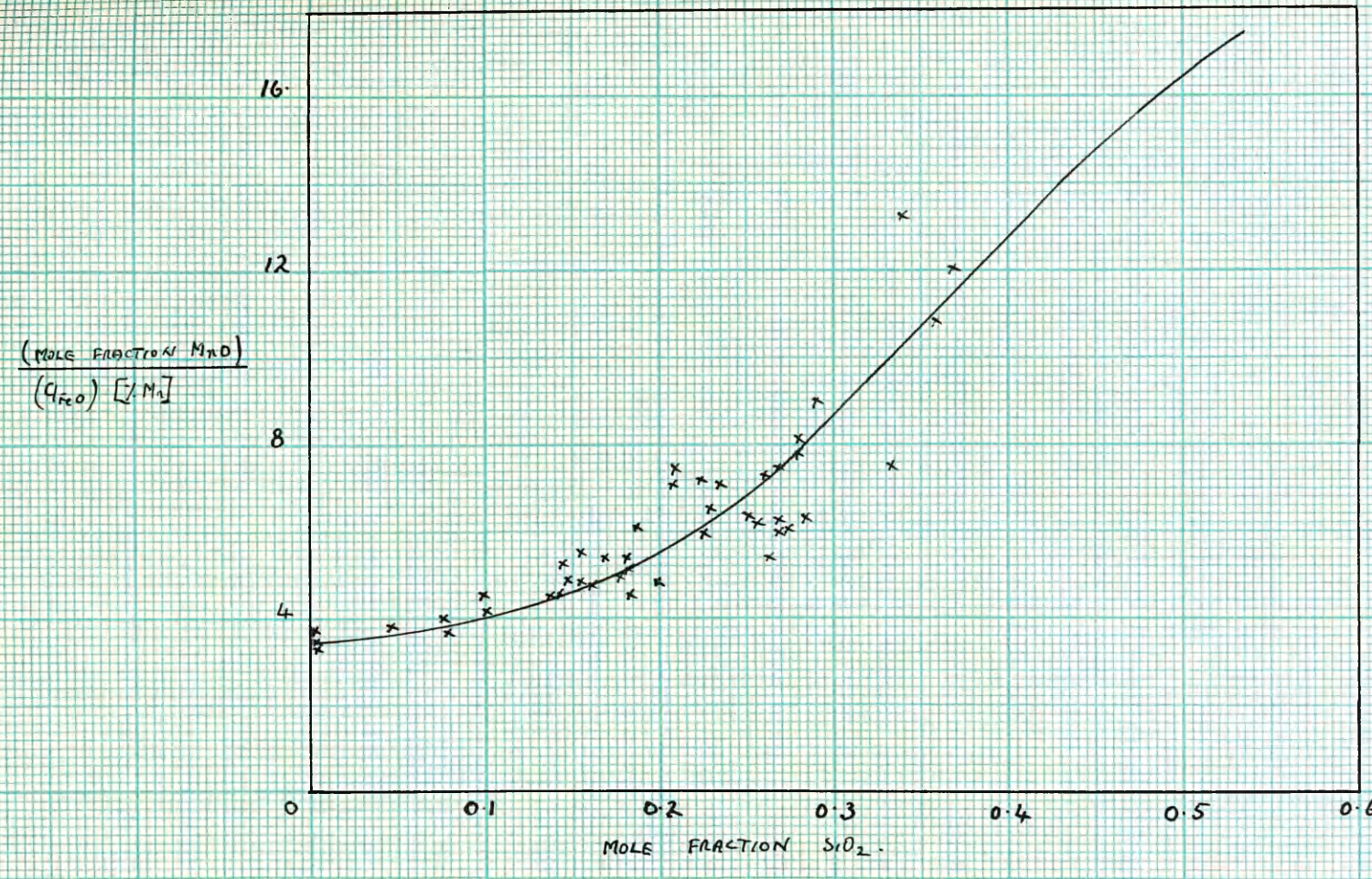


FIG. 22 GRAPH USED TO CALCULATE a_{MnO}

the supercooled liquids in the range 0 to 0·17 mole fraction silica. Since no variation of K'_{Mn} with MnO/FeO ratio was detected in the melts this activity curve should give a close approximation to a_{MnO} in this system. The data are compared with the effect of silica on a_{FeO} and a_{MnO} in the FeO/SiO_2 and $CaO-SiO_2$ systems in Fig.23. Schuhmann and Ensio(33) data have been used for the $FeO-SiO_2$ system and the activity of calcium oxide has been calculated(51) assuming a linear variation from $a_{CaO} = 1$ at $N_{SiO_2} = 0$ almost to $a_{CaO} = 0$ at $N_{SiO_2} = 0·33$ and using the data calculated by Rosenqvist(64) at the less basic compositions. Also shown are values for a_{CaO} and a_{SiO_2} at 1600°C in the system $CaO-SiO_2$ calculated by Richardson(48). The data on calcium oxide at silica contents below 42% refers to supercooled $CaO-SiO_2$ slags. The relative positions of these activity curves are in agreement with the known cation-oxygen bond strengths of calcium, manganese and iron.

The activities of silica in these systems has been calculated using the Gibbs-Duhem equation and are also shown in Fig.23. Darken(63) has published a method of applying the Gibbs-Duhem relation to ternary systems so that knowing the activity of one component that of the others can be calculated, but since this method requires extensive and precise measurements of the activity at low concentrations of ferrous oxide, it was found to be inapplicable to the results obtained in this work. Thus to obtain a_{SiO_2} in $FeO-MnO-SiO_2$ slags the approximate method used by Bell, Murad and Carter(51) has been adopted in which interpolation is made between the curves for a_{SiO_2} in the $FeO-SiO_2$ and $MnO-SiO_2$ systems according to the FeO/MnO ratio of the slag.

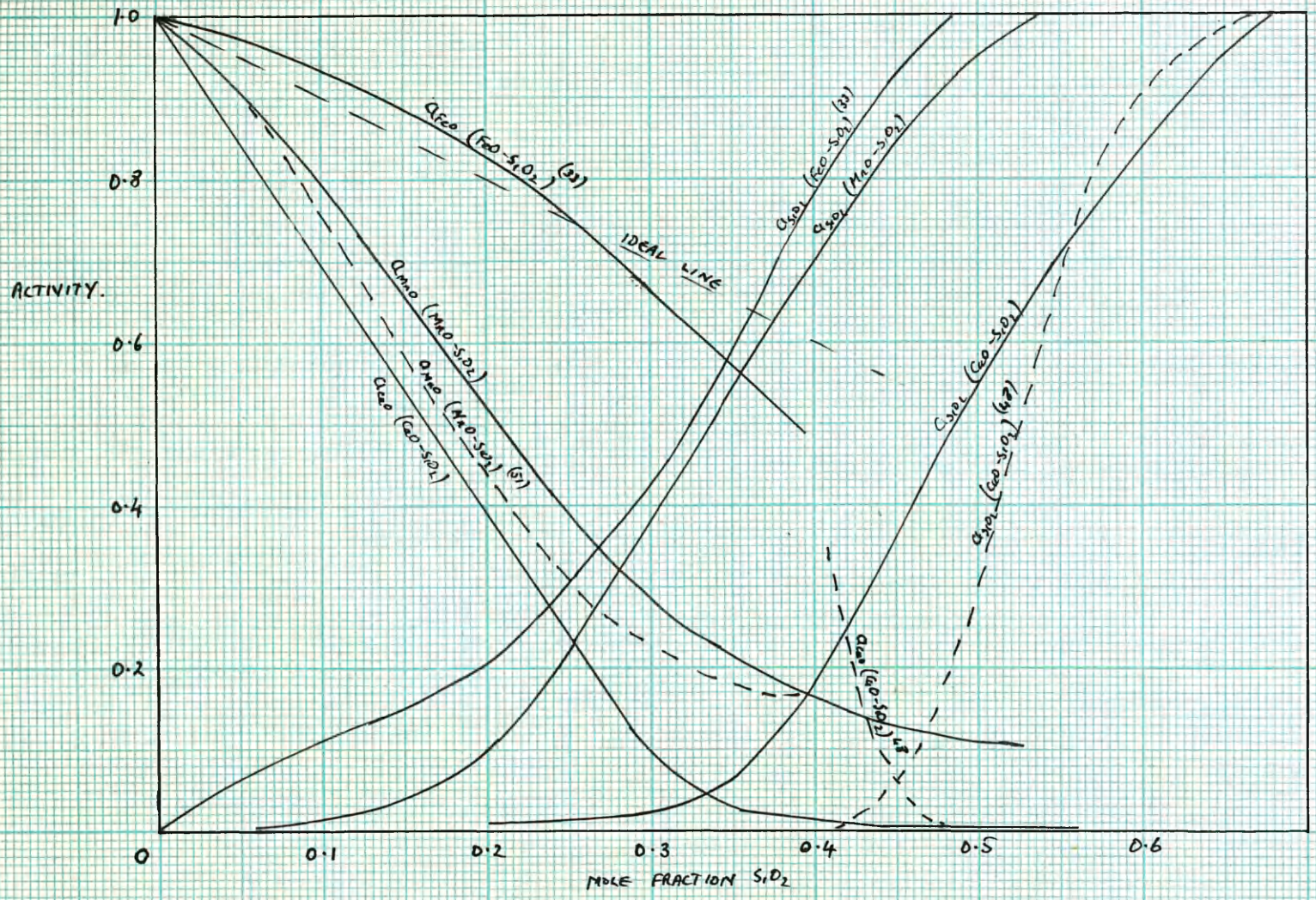


FIG 23 ACTIVITIES IN $FeO-SiO_2$, $MnO-SiO_2$, $CaO-SiO_2$ SYSTEMS.

Using the data K'_{Mn} in Fig.21 and applying it to slags a ternary system $FeO-MnO-SiO_2$ has been constructed giving the manganese contents of molten iron at 1550°C in equilibrium with these slags as a function of the slag composition (Fig.24).

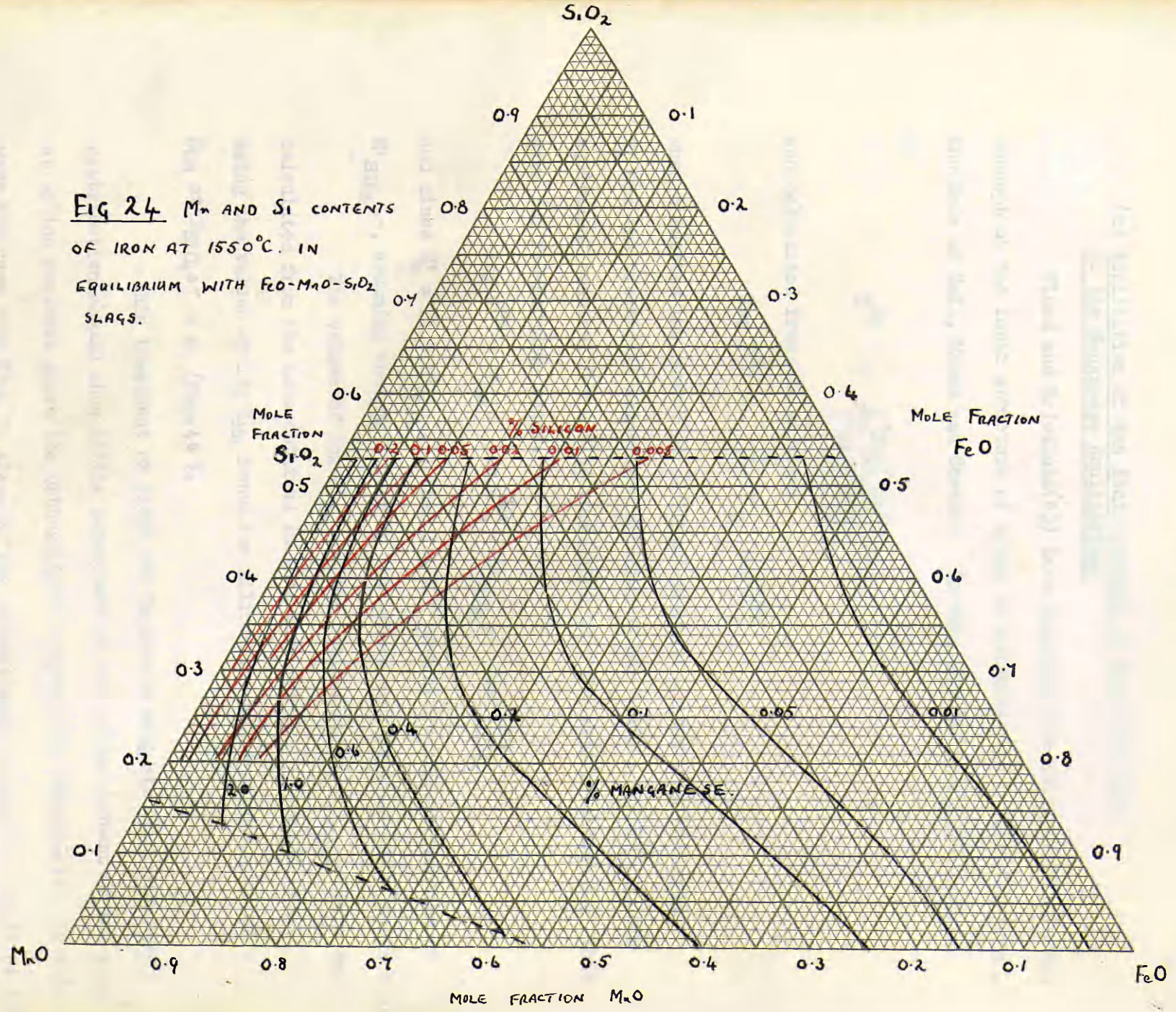


FIG 24 Mn AND Si CONTENTS OF IRON AT 1550°C. IN EQUILIBRIUM WITH FeO-MnO-SiO2 SLAGS.

(c) Application of the Ionic Concept of Slag Structure to the Manganese Equilibrium.

Flood and Grjotheim(65) have discussed the application of their concept of the ionic structure of slags to the manganese equilibrium using the data of Bell, Murad and Carter. In this discussion K_{Mn} was defined as

$$K^{Mn} = \frac{[a_{Fe}](a_{Mn^{++}})}{[a_{Mn}](a_{Fe^{++}})}$$

and calculated from the equation

$$\log K^{Mn} = \sum_{i=1}^{n} N'_i \log K^{Mn}_i$$

when n denoted the number of different kinds of anions i in the slag, N_i was the electrical equivalent fraction of the anion i and K^{Mn}_i is the equivalent constant for a slag containing only one kind of anions i. This gave for $FeO-MnO-SiO_2$ slags,

$$\log K^{Mn} = N'_{O^{2-}} \log K^{Mn}_O + N'_{SiO_4^{4-}} \log K^{Mn}_{SiO_4}$$

and since $N'_O = (1 - N'_{SiO_4^{4-}})$ then $\log K^{Mn}$ should be a linear function of $N'_{SiO_4^{4-}}$, assuming that Mg^{++} ions do not affect the distribution of manganese.

The values of $\log K'_{Mn}$ and the ionic fraction $N'_{SiO_4^{4-}}$ have been calculated from the data obtained in this work and are plotted in Fig.25 using the values of $\log K_{Mn}$ found for silica-free melts as the value of K_{Mn} at $N_{SiO_4^{4-}} = 0$. (Page 46).

This treatment of Flood and Grjotheim suggests that manganese distribution should show little dependence on the silica content of the slag at silica contents above the orthosilicate composition ($2MO.SiO_2$). If this were the case then K'_{Mn} in slags of the orthosilicate composition would be the

same as that for silica -saturated slags, i.e., in the nomenclature of Flood and Grjotheim

$$K_{Mn}^{SiO_x} = K_{Mn}^{SiO_4}$$

The results plotted in Fig.25 indicate that $K_{Mn}^{SiO_4}$ is 12 while $K_{Mn}^{SiO_x}$ was found to be 15·5 at 1550°C; this would suggest that the assumption of SiO_4^{4-} as the ionic species of silica was not strictly correct in slags with a high silica content. It is probable that in slags of $N_{SiO_2} > 0{\cdot}33$ that ions of $Si_2O_6^{4-}$ are present and also it is likely that ions of this type appear when $N_{SiO_2} < 0{\cdot}33$ and increase in proportion with increasing silica content. This change in the ionic structure of the slags would explain why K'_{Mn} at the orthosilicate composition was less than that in silica-saturated slags. Although the high electrical conductivity of liquid silicates strongly suggests an ionic structure the precise nature of the ions is not yet established.

In Flood and Grjotheim's(65) treatment of the manganese equilibrium using ions the effect of interaction between ions of the same sign has been neglected; this is probably a reasonable approach in this case but this interaction may be important in other equilibria.

The ionic concept of liquid slag structure is at present not very advanced but as information is developed on the types of ions present it should prove a useful tool in the understanding of slag-metal reactions. As used at present it is similar to the methods used by Schenck and White in which slag components were considered to be neutralised by combination whereas in the application of ionic structure by Flood(47), Temkin(46) and

Herasymenko(45) ions are considered to be rendered inactive by interaction with ions of opposite sign.

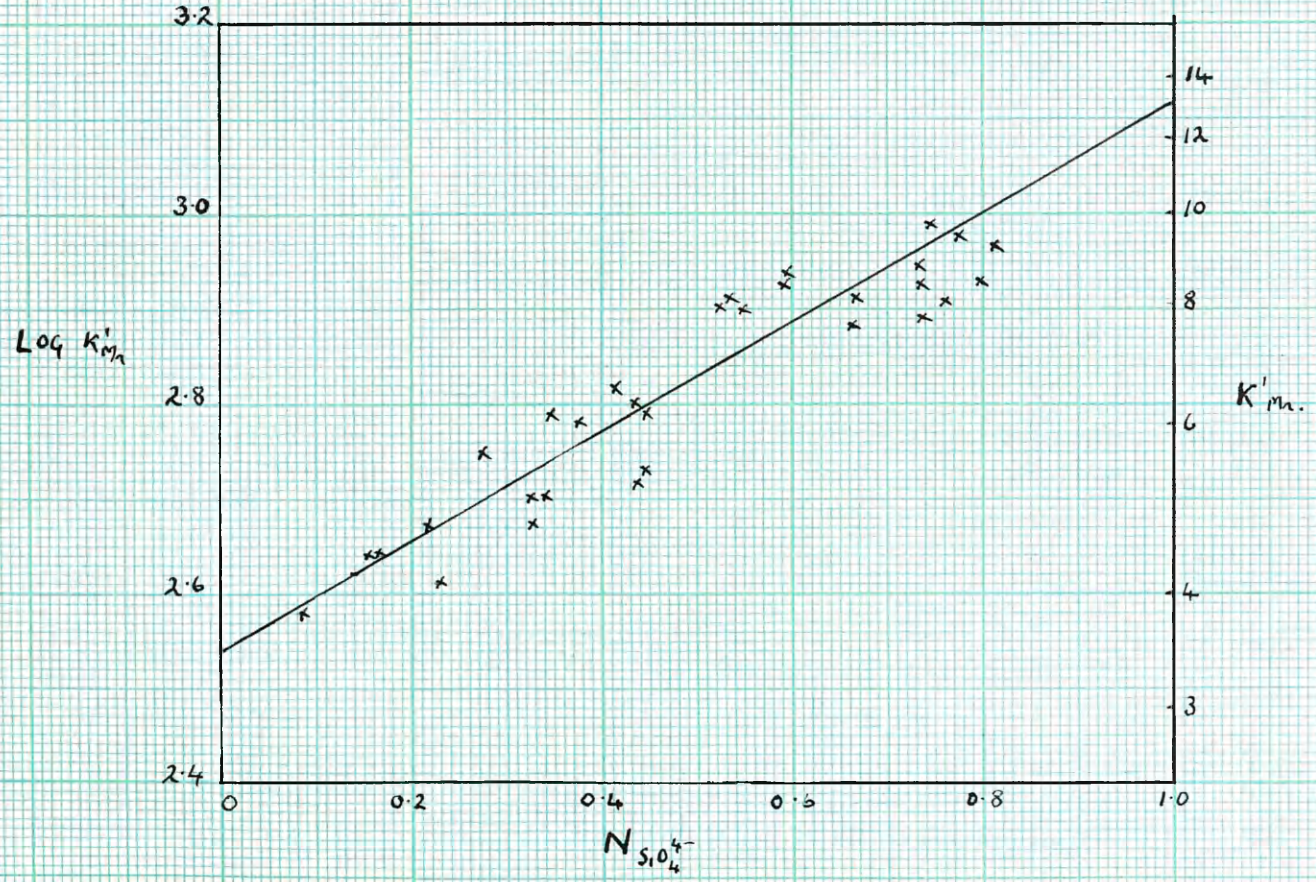


FIG 25 APPLICATION OF IONIC THEORY TO RESULTS ON MANGANESE EQUILIBRIUM.

(d) Silicon Equilibrium.

In the discussion on silica-saturated melts the silicon equilibrium has been represented as

$$K'_{Si} = [\%Si][\%O]^2 = 1{\cdot}1 \times 10^{-5} \text{ at } 1550^{\circ}C \quad (35)$$

since the activity of silica was unity. But in the melts made in magnesia crucibles the activity of silica was not unity and before K'_{Si} can be found for these melts the activity of silica in the slags must be determined, i.e.,

$$K'_{Si} = \frac{[\%Si][\%O]^2}{a_{SiO_2}}$$

Chipman and Gokcen(35) have found that in the range of silicon contents 0·01/5% that the product $[\%Si][\%O]^2$ is constant but that this does not necessarily mean that solutions of silicon and oxygen in liquid Fe-O-Si alloys obey Henry's Law in this range. They have found that f_O is reduced by silicon and that in dilute solutions f_{Si} increases with concentration but that in respect to the silicon-oxygen equilibrium within the range 0·01/1% that these effects are approximately compensating. Using silica saturated slags or H_2/H_2O mixtures in silica crucibles the maximum oxygen content of the metal is limited to that in equilibrium with silica saturated slags and the effect of high oxygen contents on the equilibrium cannot be studied. In this work unsaturated FeO-MnO-MgO-SiO_2 were used and higher oxygen contents were obtained, but this also meant low silicon contents and the errors in analysis resulting from this .

The activities of silica in the slags were calculated from the curves for a_{SiO_2} in MnO-SiO_2 and FeO-SiO_2 shown in Fig.23 by interpolation between these curves according to the FeO and MnO contents of the slag.

Using this method the magnesia is treated as a diluent and the values of a_{SiO_2} are therefore only approximate. Table 10 gives the values found by this method together with the silicon and oxygen contents of the metal to which they refer. From this data values of K'_{Si} have been calculated and are given in Table 10. These results indicate that when the oxygen content of the metal was below 0·05% the values of K'_{Si} were of the same order as those found for silica-saturated FeO-MnO-SiO_2 slags, but as the oxygen content of the iron increased the ratio K'_{Si} increased rapidly till at oxygen contents above 0·1% it was of the order of 20 times K'_{Si} for silica saturated slags. In view of the method used to assess the value of a_{SiO_2} and of the large effect on K'_{Si} of small errors in the analysis at the low silicon contents a fairly wide scatter in the results might be expected. Nevertheless the deviations in K'_{Si} showed a trend, the largest deviations being at high oxygen contents; from this it appeared that oxygen was affecting the activity of silicon in Fe-O-Si alloys. If a factor taking into account this effect is introduced into the expression for K'_{Si} then the relation

$$f^{\circ}_{Si}\frac{[\%Si][\%O]^2}{a_{SiO_2}} = 1{\cdot}1 \times 10^{-5} \quad \text{at } 1550^{\circ}C.$$

should be satisfied, f°_{Si} being the effect of oxygen on the activity coefficient of silicon in Fe-O-Si alloys. The standard state of silicon in this expression is 0·1% solution of silicon in liquid iron. From this expression values of f°_{Si} can be found for all the melts made which although subject to some error should show the trend in the effect of oxygen on the activity of silicon.

TABLE 10.

Silicon Equilibrium.

Melt No.	Mole Fraction SiO_2	a_{SiO_2}	[Si] wt. %	[O] wt. %	$\frac{[\%Si][\%O]^2}{a_{SiO_2}} \times 10^5$	f^o_{Si}
3	0.079	0.08	< 0.001	0.134	22	< 0.1
4	0.076	0.07	0.002	0.097	26	< 0.1
5	0.100	0.05	0.005	0.050	24	< 0.1
6	0.157	0.08	0.008	0.0495	28	< 0.1
7	0.142	0.09	0.002	0.078	15	0.1
8	0.183	0.13	0.003	0.063	9	0.15
10	0.211	0.17	0.007	0.075	22	< 0.1
15	0.286	0.34	0.018	0.0238	3.0	0.4
16	0.200	0.15	0.004	0.051	6.8	0.2
18	0.267	0.30	0.004	0.040	2.1	0.6
21	0.160	0.10	0.005	0.021	2.0	0.6
26	0.180	0.14	0.006	0.085	31	< 0.1
27	0.141	0.11	0.004	0.0965	33	< 0.1
28	0.290	0.36	0.042	0.0103	1.24	1.0
29	0.218	0.20	0.003	0.085	10.5	0.1
30	0.224	0.21	0.007	0.059	11	0.1
31	0.271	0.32	0.003	0.046	1.95	0.6
32	0.229	0.17	0.002	0.0297	1.1	1.0
34	0.279	0.32	0.030	0.0185	1.6	1.0
37	0.273	0.32	0.002	0.0590	2.1	0.6
39	0.102	0.08	0.002	0.083	17	0.1
41	0.173	0.13	0.002	0.088	12	0.1
42	0.340	0.54	0.79	0.0028	1.17	1.0
48	0.280	0.34	0.007	0.042	3.5	0.5
53	0.281	0.32	0.020	0.0145	1.3	1.0
54	0.274	0.30	0.005	0.0505	4.2	0.3
55	0.336	0.51	0.014	0.044	5.3	0.2
57	0.233	0.23	0.005	0.067	9.5	0.15
58	0.252	0.26	0.005	0.055	5.5	0.2
59	0.234	0.20	0.005	0.040	4.1	0.3
61	0.265	0.28	0.004	0.049	3.5	0.3
65	0.36	0.62	0.026	0.018	1.36	1.0

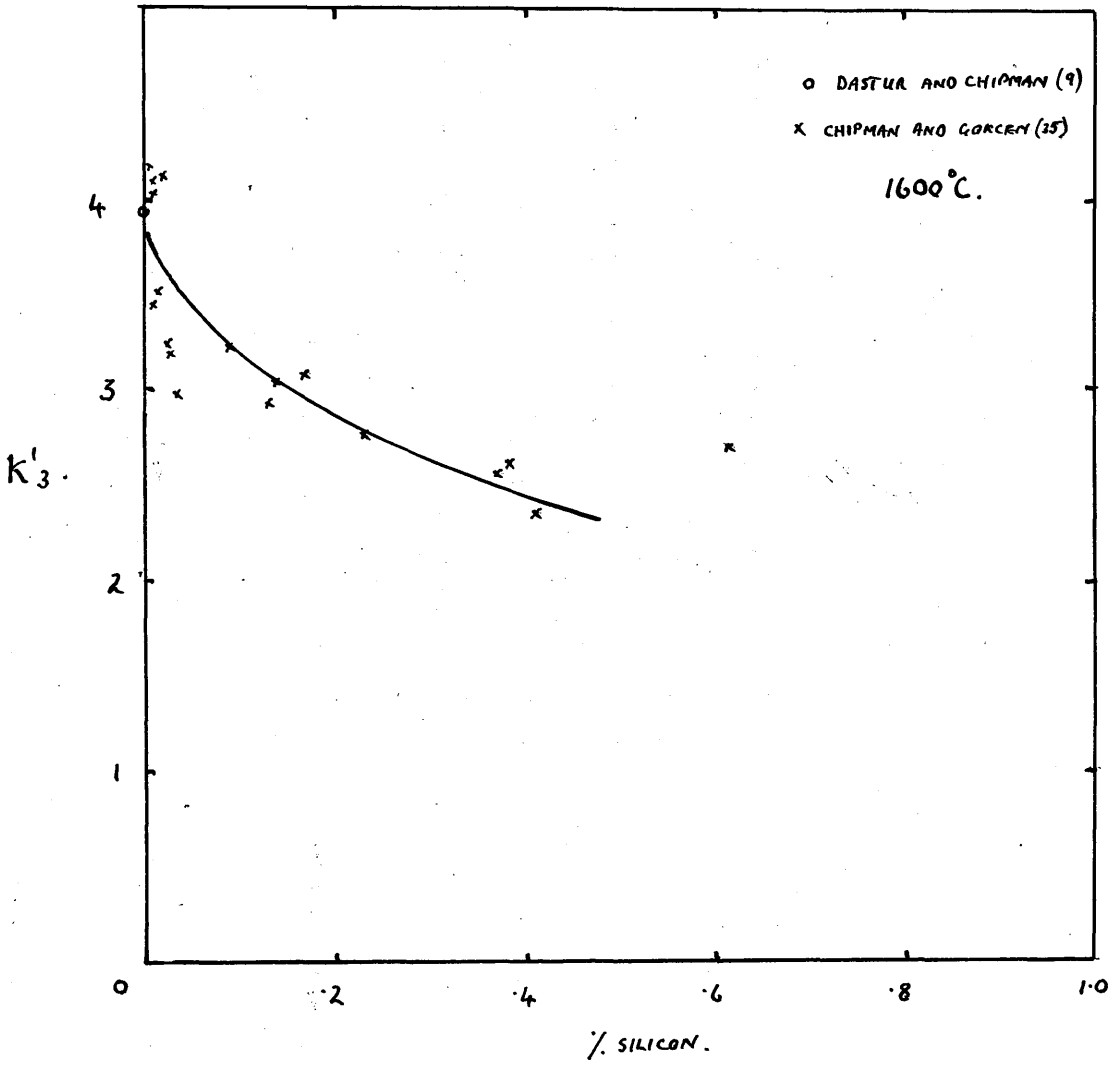


FIG 26a. EFFECT OF SILICON ON $k'_3 = \frac{(H_2O)}{(H_2)[\underline{O}]}$

Chipman and Gokcen from their results on the H_2/H_2O-Fe-Si-O equilibrium have calculated a similar effect using Wagner's(68) method of calculating the activities of the other components in a ternary system from a knowledge of one. Chipman and Gokcen(35a) withdrew this calculation in view of the fact that the value of the equilibrium constant $K'_3 = \frac{(H_2O)}{(H_2)[\%O]}$ extrapolated to zero concentration of silicon did not agree with that obtained by Dastur and Chipman(9), but qualitatively stated that the activity coefficient of oxygen in molten iron is reduced by the presence of silicon. From this it can be concluded that oxygen should affect the activity coefficient of silicon, a result which has been confirmed in the present work. In Fig.26 a graph has been plotted showing the effect of oxygen on f°_{Si} and indicating that at oxygen contents above 0·06% at 1550°C this effect is large. These results tend to confirm the first calculations of Chipman and Gokcen and examination of their data indicates that the values of K' at low silicon contents when extrapolated to zero silicon content (Fig.26a) gives a value for K_3 agreeing reasonably well with that of Dastur and Chipman. In view of this it appears that the original calculations of Chipman and Gokcen on the activity of silicon in Fe-O-Si alloys are reasonably accurate.

The silicon content of molten iron in equilibrium with FeO-MnO-SiO_2 slags can be calculated using the data on a_{FeO} and a_{SiO_2} in these slags with the value of K'_{Si} and assuming at 1550°C

$$[O] = 0{\cdot}19\ a_{FeO}$$

$$K'_{Si} = \frac{[\%Si][\%O]^2}{(a_{SiO_2})} = 1{\cdot}1 \times 10^{-5}$$

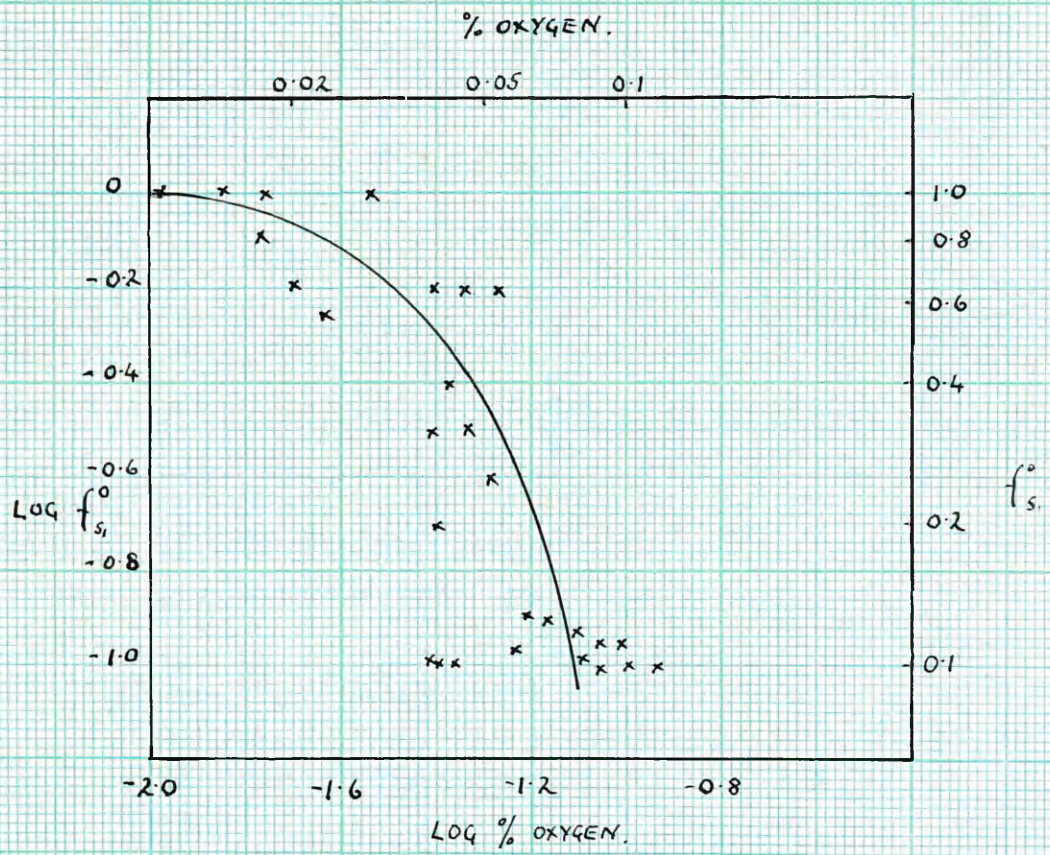


FIG 26 EFFECT OF OXYGEN ON ACTIVITY COEFFICIENT OF SILICON IN IRON.

$$[Si] = \frac{1{\cdot}1\ (a_{SiO_2}) \times 10^{-5}}{0{\cdot}036(a_{FeO})^2}$$

$$= \frac{3{\cdot}1\ a_{SiO_2}}{(a_{FeO})^2} \cdot 10^{-4}$$

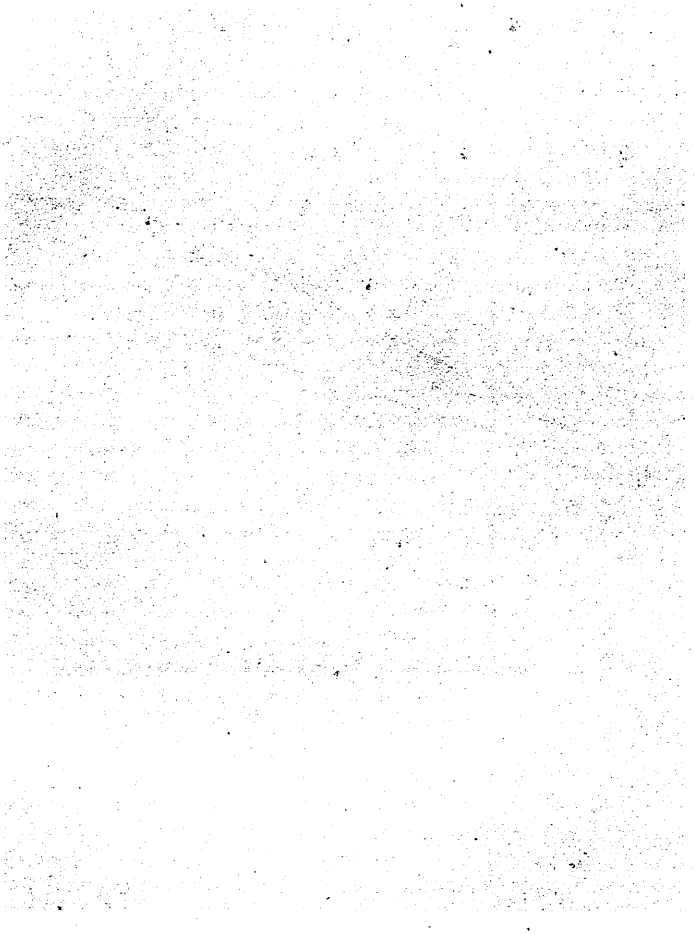
At silicon contents less than 0·01% a correction must be made for the effect of oxygen on the activity of silicon.

Using these relations lines of equal silicon content have been plotted on the ternary system FeO-MnO-SiO_2 in Fig.24.

(e) Silicon-Manganese-Oxygen Equilibrium in Molten Iron.

The investigations of Hilty and Crafts(29) and Korber and Oelsen (38) have shown that in the presence of manganese, silicon has a much greater effect in reducing the solubility of oxygen in liquid iron than when used alone. The effect of silicon in the presence of manganese is shown in Fig.27 where the oxygen content has been plotted for constant manganese contents with varying silicon concentrations. This indicates the larger effect which silicon has in the presence of manganese than when used alone. Fig.27 was plotted using the data in Figs.14 and 24; the same data has also been used in Fig.28 to show the effect of varying manganese concentrations at constant silicon contents. Similar diagrams have also been constructed by Hilty and Crafts and these are compared with the present work in Figs.28 and 29, which show that, although manganese reduced the solubility of molten iron for oxygen in the presence of silicon, this effect was not as large as found by Hilty and Crafts. The discrepancies between Hilty and Crafts and this work can only be attributed to the effect of the different experimental techniques. As has already been mentioned the composition of the slags with which Hilty and Crafts' melts were in equilibrium was uncertain, the equilibrium being probably between the metal and a slag which had soaked into the alumina crucibles. This would probably tend to reduce a_{FeO} in these slags, hence reducing the oxygen content of the melts. Also the large reduction in the oxygen solubility of molten iron due to manganese and silicon found by Hilty and Crafts would indicate that a_{FeO} was lowered by the addition of MnO to an $FeO\text{-}SiO_2$ slag, an effect

which would not be expected in the light of the work of Taylor and Chipman(13) and Winkler and Chipman(28), and which has not been found in this work.



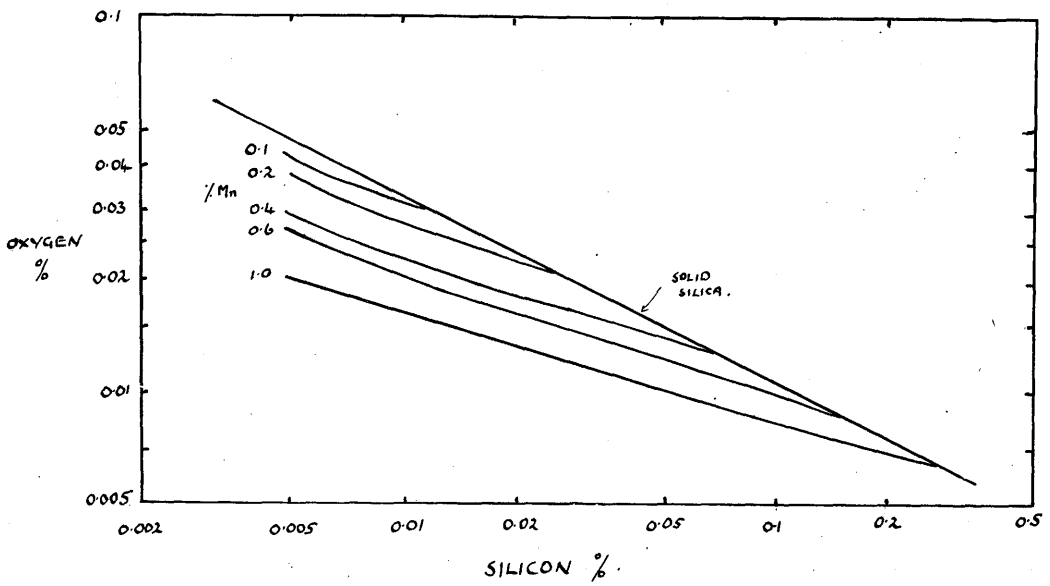


FIG 27 EFFECT OF MANGANESE AND SILICON ON THE OXYGEN CONTENT OF IRON AT 1550°C.

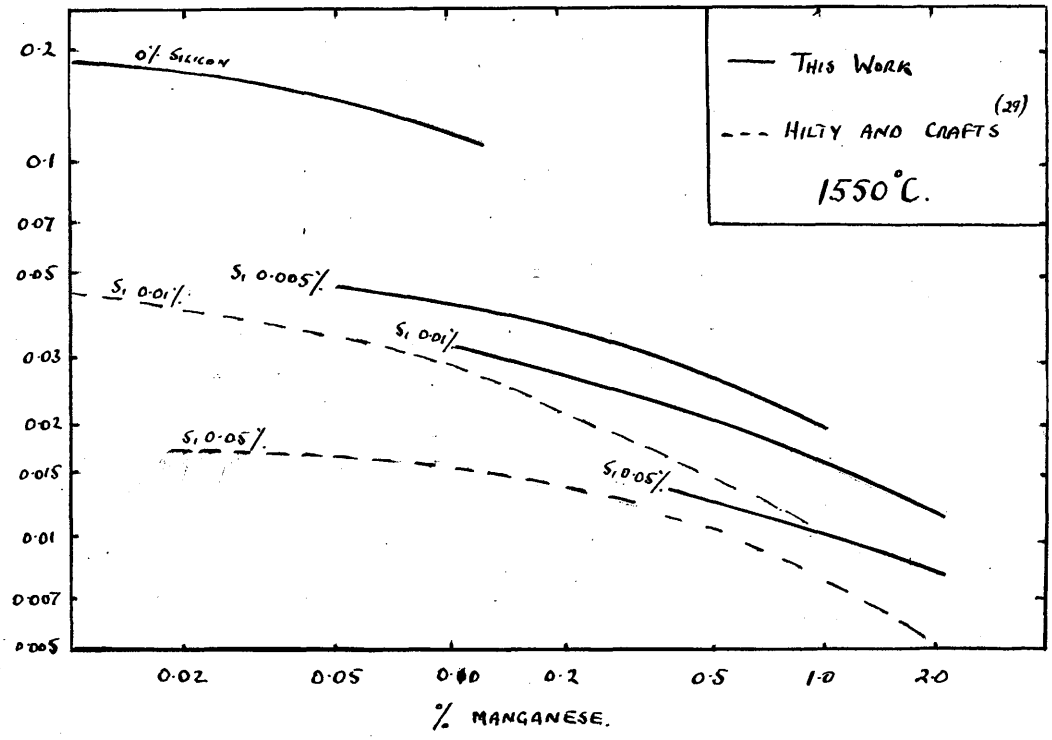


FIG 28 MANGANESE - OXYGEN EQUILIBRIUM IN PRESENCE OF SILICON

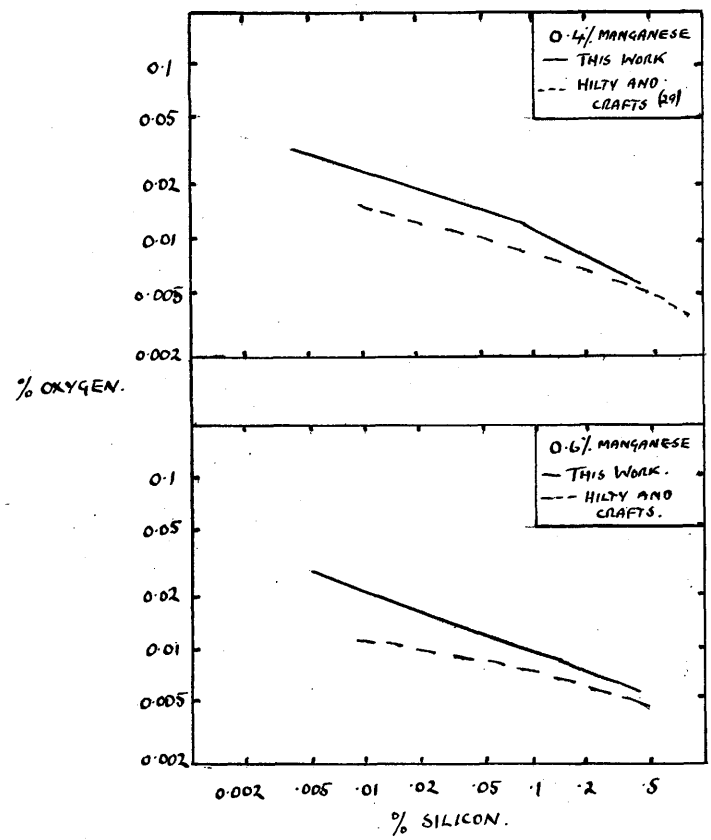


FIG 29 SILICON - OXYGEN EQUILIBRIUM IN PRESENCE OF MANGANESE.

APPLICATION OF RESULTS TO DEOXIDATION OF IRON.

V. Application of Results to Deoxidation of Iron.

1. Deoxidation by Manganese alone.

The effect of manganese on the oxygen content of liquid iron can be deduced from the value of K_{Mn} and from the fact that ferrous oxide behaves ideally in an FeO-MnO-slag.

At 1550°C

$$K_{Mn} = \frac{(\%MnO)}{(\%FeO)[\%Mn]} = 3{\cdot}6$$

$$\frac{[\%O]}{(\%FeO)} = 0{\cdot}0019$$

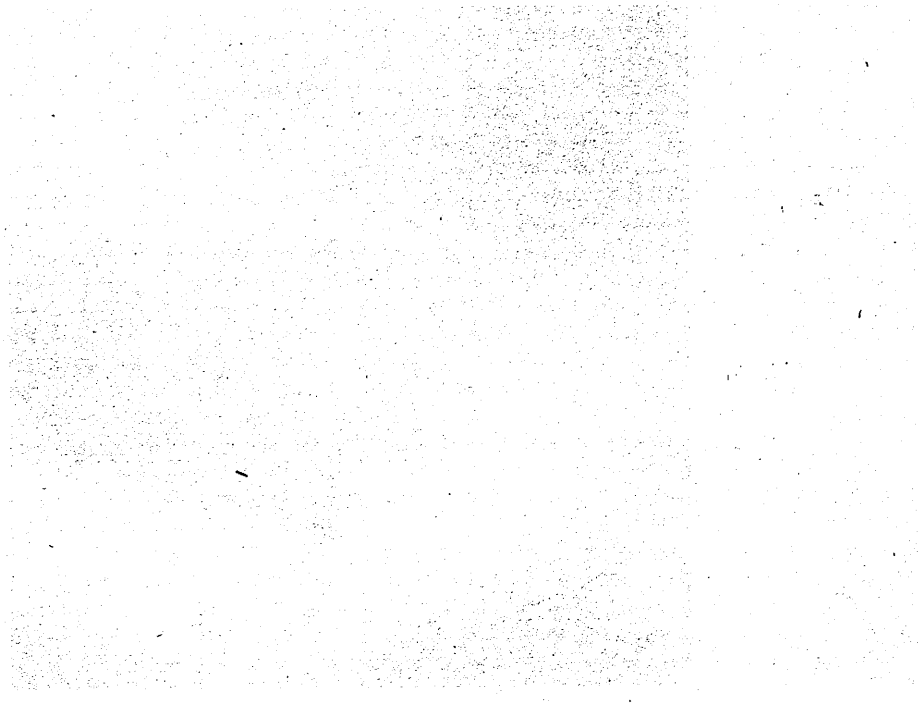
Hence $$\frac{(100 - \frac{[O]}{0{\cdot}0019})0{\cdot}0019}{[\%O]\,[\%Mn]} = 3{\cdot}6$$

or $$[\%O] = \frac{0{\cdot}19}{3{\cdot}6[\%Mn] + 1}$$

This equation only holds when liquid FeO-MnO products are formed, and the composition of these products can be readily calculated from the value of K_{Mn}. Liquid FeO-MnO products are only formed when the concentration of manganese in the iron at 1550°C is below 0·12%(26), at which the oxygen content is 0·133%. Further additions of manganese above 0·12% lower the oxygen content of the metal but give products consisting of FeO-MnO solid solution. The composition of these products and the oxygen content of the metal with which they are in equilibrium can be calculated from the FeO-MnO equilibrium diagram and have already been indicated in Fig.12.

The manganese addition required to produce a given amount of deoxidation, within the limits of its deoxidising power, can be calculated from a knowledge of the composition of the deoxidation products. This calculation has been made for 1550°C and is shown in Fig.30 as the amount

of manganese to be added to oxygen saturated iron to give oxygen contents from 0·19%.to 0·13% and also showing the residual manganese content of the metal. In this range of manganese and oxygen contents the deoxidation products are liquid. Manganese is thus not a very efficient deoxidising element when used alone; also since the oxygen content of molten steel at tap is seldom above 0·13% at 1550°C or 0·14% at 1600°C, manganese deoxidation will produce solid products.



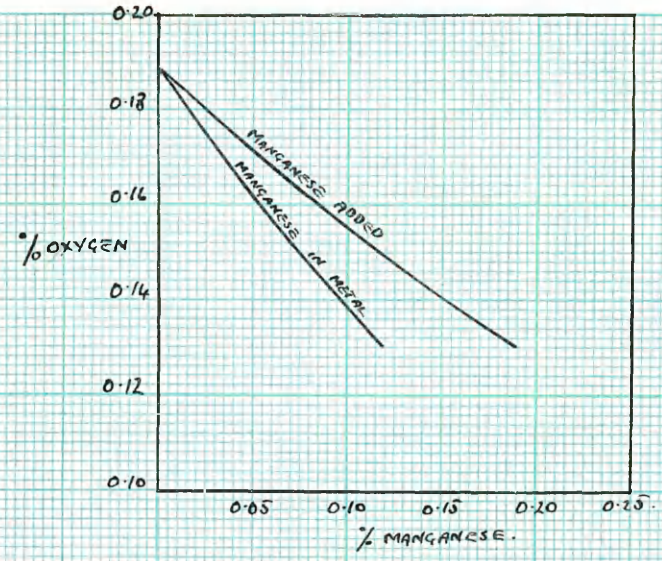


FIG 30 DEOXIDATION BY MANGANESE.

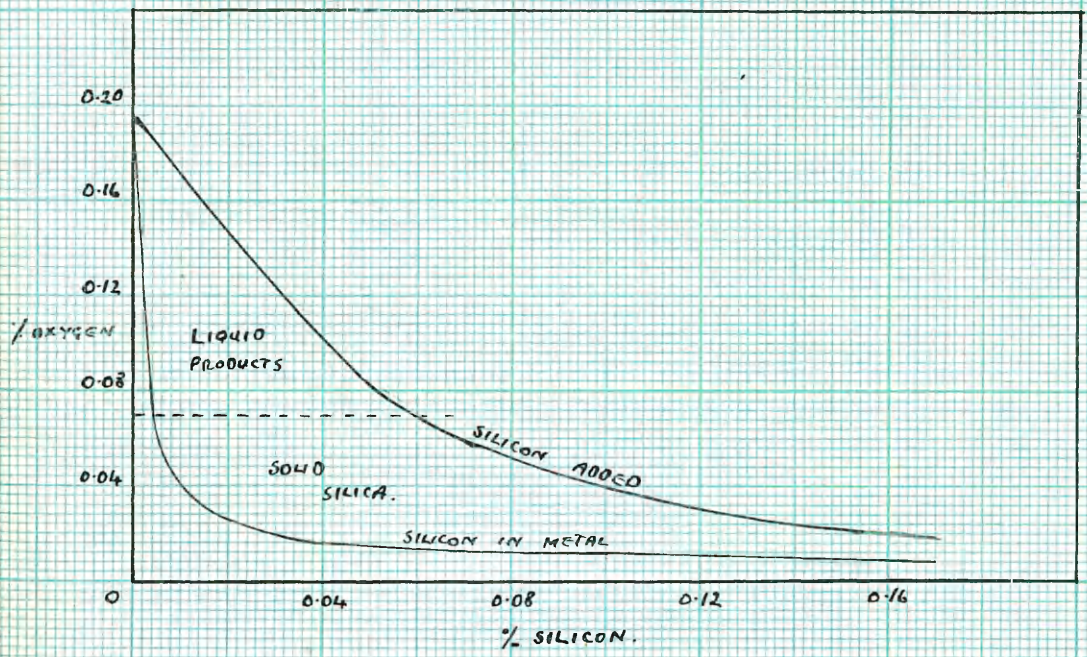


FIG 31 EFFECT OF SILICON ADDITIONS ON THE OXYGEN CONTENT OF OXYGEN-SATURATED IRON AT 1550°C.

11. Deoxidation by Silicon.

The effect of silicon on the oxygen content of molten iron can be deduced directly from the relation

$$K_{Si} = [\%Si][\%O]^2 = 1{\cdot}1 \times 10^{-5} \quad \text{at} \quad 1500°C$$

In contact with a silica-saturated $FeO\text{-}SiO_2$ inclusion the oxygen content of molten iron at 1550°C is 0·074% at 1550°C. The silicon content calculated from K'_{Si} would be 0·002% under these conditions; but as has been indicated it is doubtful if this value of K'_{Si} holds at oxygen concentrations of this order and the silicon content of the iron may be higher, probably of the order of 0·005%.

If silicon is added to oxygen saturated molten iron at 1550°C liquid products, $FeO\text{-}SiO_2$ in composition, are produced till the oxygen content is reduced to 0·074%, further additions of silicon produce solid silica as the deoxidation product. Using the data on K_{Si}(35a) and the knowledge of the deoxidation products a diagram has been constructed relating the amount of silicon added to the oxygen and silicon contents of the metal and is shown in Fig.31. This indicates that the first additions of silicon reduce the oxygen concentration rapidly but after 0·16% silica has been added the rate of oxygen removal with increasing silicon decreases rapidly. After 0·06% silicon has been added the deoxidation products consist of solid silica. The oxygen content of oxygen-saturated iron at 1550°C can be reduced to 0·01% by adding 0·2% silicon, 0·12% of which remains dissolved in the iron.

Silicon is a powerful deoxidising element but it has the disadvantage that where the products are solid silica they are difficult to remove from the metal as they rise very slowly because of their size. One of the main uses of silicon as a deoxidiser is in "blocking" a heat by reducing the oxygen content of a melt and so preventing further carbon oxidation.

111. Deoxidation by Manganese and Silicon.

Manganese and silicon when used together have a much greater deoxidising effect than when used singly. Fig.32 shows a comparison of the deoxidising powers of manganese, silicon, silicon with 0·6% manganese as found in the present work and aluminium(69)(70) at 1550°C. This shows that manganese with silicon is a much better deoxidiser than manganese alone and a little better than silicon alone but not so effective as aluminium. Although this increase in deoxidising power is an advantage a further one is that within the range shown the products are liquid whereas those of aluminium and silicon are solid silica or alumina. Part of the $FeO-MnO-SiO_2$ phase diagram is given in Fig.33, the isothermals in the $FeO-MnO-2FeO.SiO_2-2MnO.SiO_2$ part being taken from Carter, Murad and Hay(22) while the eutectic trough indicated near the $MnO-SiO_2$ side of the system at 40% silica was found by Murad(50). This diagram shows that it is possible to produce low melting, very fluid deoxidation products at low oxygen contents. Two areas, A and B, are marked where the deoxidation products are fluid at steelmaking temperatures and in equilibrium with iron containing less than 0·5% manganese, 0·05% silicon and 0·04% oxygen.

Theoretically it should be possible to produce these liquid inclusions by adding calculated amounts of ferro-silicon and ferromanganese. In practice this is not possible since it is unlikely that the solid silica and manganous oxide rich inclusions produced from the ferrosilicon and ferromanganese would come into contact and flux with each other to give a homogeneous deoxidation product. Thus in deoxidation it would be much better to use a silicon manganese alloy of a predetermined composition which would produce deoxidation products of the desired type directly.

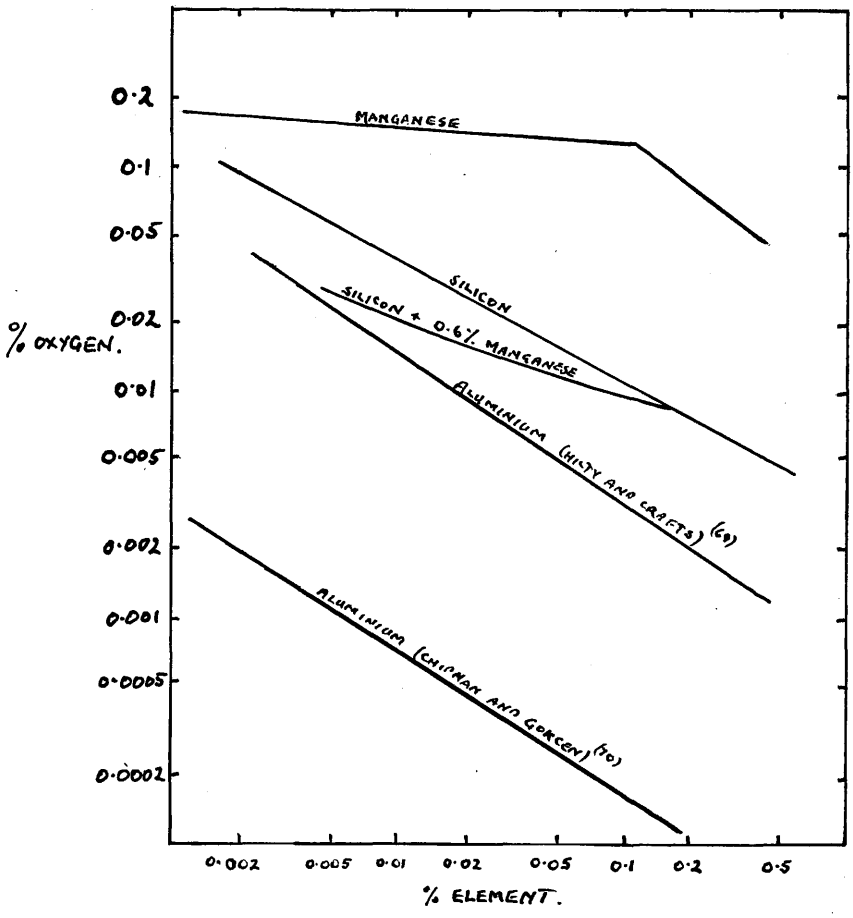


FIG 32 COMPARISON OF DEOXIDISING POWERS OF ELEMENTS AT 1550°C.

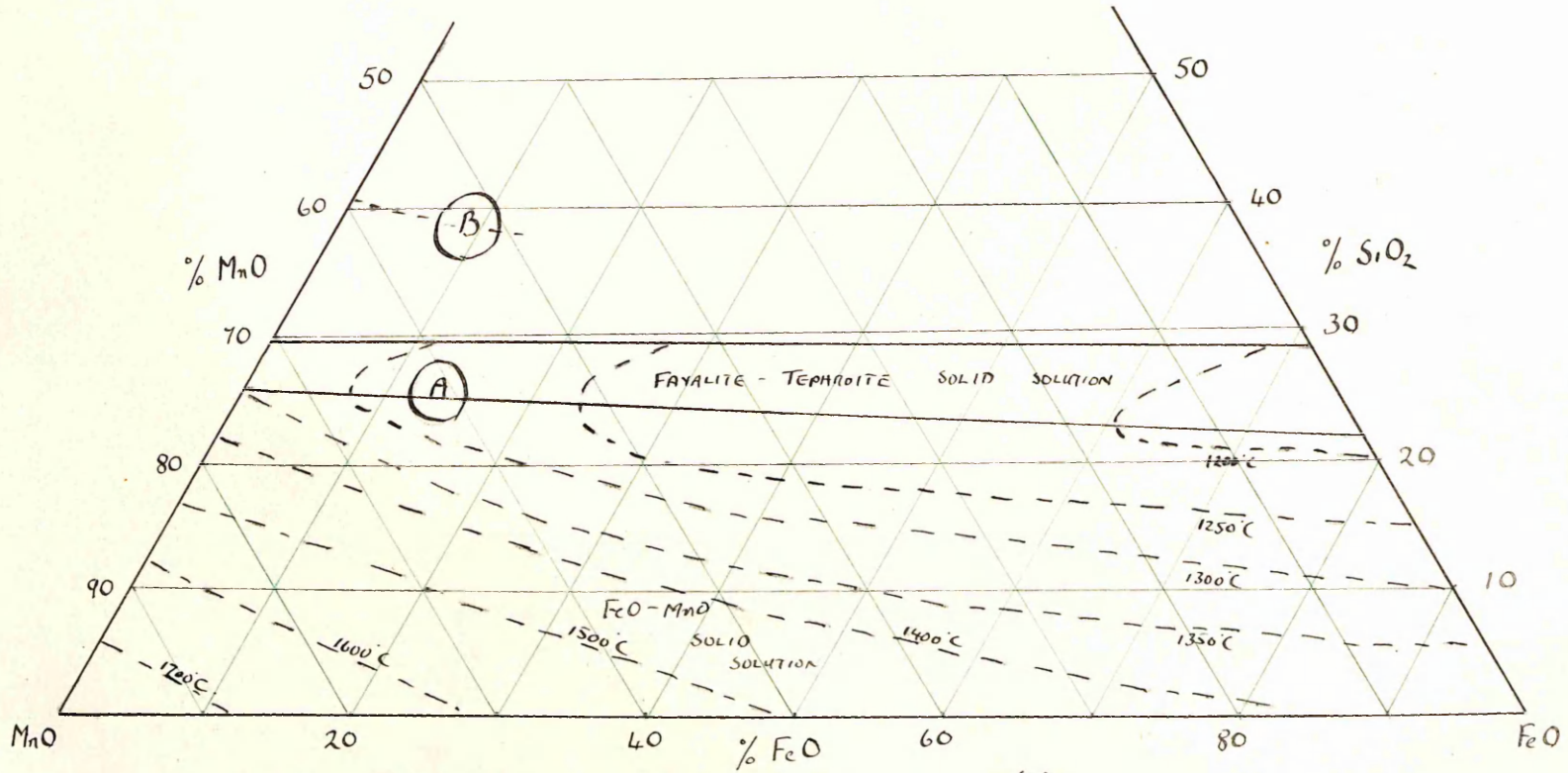


FIG 33 $FeO - MnO - SiO_2$ PHASE DIAGRAM (21)

From Fig.33 desirable compositions of inclusions are shown in Table 11.

Table 11.
Composition of low melting MnO-FeO-SiO_2 Inclusions.

	Deoxidation product %. SiO_2	MnO	FeO.	Melting point approx.	Mn/Si ratio in product.	Metal in equilibrium with product at 1550°C. Mn%	Si%	O%
A	26	60	14	1280°C	3·6	0·5	0·005	0·035
B	40	52	8	1250°C	2·2	0·5	0·02	0·025

From this data it can be seen that the major part of the oxygen removal is performed by the silicon since the manganese to silicon ratio is much higher in the metal than in the deoxidation product. If a silicon-manganese alloy of $\frac{Mn}{Si} = \frac{4}{1}$ ratio were used then extra manganese would require to be added to account for solution of manganese in the iron. The amount of alloy to be added can be calculated, for example taking a molten iron containing at 1550°C 0·14% oxygen, 0·1% manganese and using a silica-manganese alloy of 70% manganese and 20% silicon.

Taking deoxidation product as 40% SiO_2, 52% MnO, 8% FeO containing 35% oxygen

$$\text{Silicon to be added} = \frac{(0{\cdot}14 - 0{\cdot}03)}{0{\cdot}35} \times 0{\cdot}185 + 0{\cdot}02 = 0{\cdot}08\%$$

$$\text{Silico-manganese to be added} = 0{\cdot}40\%$$

$$\text{Manganese to be added} = \frac{(0{\cdot}14 - 0{\cdot}03)}{0{\cdot}35} \times 0{\cdot}40 + 0{\cdot}4 = 0{\cdot}52\%$$

$$\text{Additional manganese required } [0{\cdot}52 - (0{\cdot}40 \times 0{\cdot}7)] = 0{\cdot}24\%$$

or 0·32% of 75% ferro-manganese.

From this calculation it would appear to be better to use an alloy with a higher manganese to silicon ratio than in the usual silico-manganese. A silicospiegel of 25-30% manganese, 5% silicon might be a better deoxidising addition than silico-manganese, provided that a small increase in carbon is of no great consequence.

After the deoxidation by silico-manganese, further deoxidation can be carried out by ferrosilicon followed by aluminium but this would be done with the production of solid silica and alumina. Deoxidising first with silico-manganese reduces greatly the amount of silicon and aluminium to be added.

A C K N O W L E D G E M E N T.

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